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OFFICIAL PUBLICATION OF THE PROCEEDINGS AMERICAN ASSOCIATION OF TEXTILE CHEMISTS AND COLORISTS

American Dyestuff Reporter was founded in 1917 and the Textile Colorist and Converter (formerly Textile Colorist) was incorporated with it in January, 1949. Published every other Monday by the HOWES PUBLISHING COMPANY, INC., 44 E. 23rd Street, New York 10, N. Y. C. R. Howes, President; Ernest J. Finan, Executive Vice-President; Norman A. Johnson, Vice-President & Treasurer; Myron D. Reeser, Vice-President; C. Essenbreis, Secretary.

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AMERICAN
DYESTUFF REPORTER

Devoted to Textile Chemistry
BLEACHING • DYEING • PRINTING • FINISHING

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AMERICAN
DYESTUFF REPORTER

VOLUME 43 AUGUST 16, 1954 NUMBER 17

HISTORICAL NOTES ON THE WET-PROCESSING INDUSTRY

V—SIR WILLIAM PERKIN

SIDNEY M EDELSTEIN

Dexter Chemical Corporation

This is the fifth in a series of historical articles which the textile chemist and colorist will find of interest.

The author, a prominent science historian, is the founder of an outstanding collection of great works, documents and letters in the history of chemistry and related sciences.

Articles and illustrations in this series are from the author's library.

A RECENT notice in this journal concerning the proposed celebration in 1956 of the centenary of Perkin's discovery of mauve sent me rummaging through my library for the answer to many questions. How was this discovery and this man looked upon on the occasion of the 50th anniversary? How quick did the world realize the importance of Perkin's discovery. What manner of man was Perkin? Each question brought forth many more — a veritable chain reaction.

One scarce little volume particularly piqued my curiosity for it was entitled "Jubilee of the Discovery of Mauve and of the Foundation of the Coal Tar Color Industry" by Sir W H Perkin, FRS, DSc, LLD, PhD, Dr.Ing *(1)*. This book was published on the occasion of the 50th anniversary of Perkin's discovery and tells of the great celebration which was held at that time in Perkin's honor in England and in America. The binding itself tells a story for this quarto volume was bound in cloth dyed with Perkin's mauve. The back, exposed to the light of half a century, is almost white. The sides, hiding in the darkness of library shelves, is still a brilliant purple.

At the end of the book there are listed members of an international committee which had been set up for the celebration. Many of these names are remembered by us as the "giants" of the educational and scientific world of Europe and America. Among the American members listed are Baekeland, Wilder Bancroft, Marston T Bogert, Nicholas Murray Butler, Chittenden of Yale, Charles Herty, J M Matthews, Ira Remsen, J Takamine, H W Wiley, Woodrow Wilson, as well as our association's founder, Louis A Olney, and our well-loved Alan Claflin, who died this year.

The main celebration was held in London at the Royal Institution on Thursday, July 26, 1906, with a fine banquet during the evening at the Hotel Metropole. Present at the celebration were representatives of the important scientific societies of England, France, Germany, Austria, Switzerland and the United States. Even representatives of the great German dyestuff companies were present to pay their respects to Perkin.

The spot chosen for the main celebration was of particular historical significance, for it was in 1825 at the Royal Institution that Michael Faraday had first discovered benzene, the basic coal tar chemical and the starting point for Perkin's mauve. On a table before the distinguished gathering sat the original specimen of benzene which Faraday had discovered. During the celebration the now famous portrait of Perkin by Cope and the beautiful bust by Pomeroy were unveiled.

While it is particularly interesting to read the speeches which the German representatives delivered in paying homage to the greatness of England and Perkin just eight years before the outbreak of the First World War, the sentiments of all the speeches of that day were best summed up in the words of the American representative, Leo Baekeland:

> "On behalf of the chemists in the United States of America I have come to congratulate you on the eminent services you have rendered to chemical science, and to chemical industry, for the greater benefit of mankind. On this day, when the whole scientific world remembers your brilliant and useful career, we express the sincere hope that your noble life may continue for many years more as an example to every chemist, and as an inspiration for further research work to the younger generation."

Figure 1
Perkin at the age of 22 (1860)

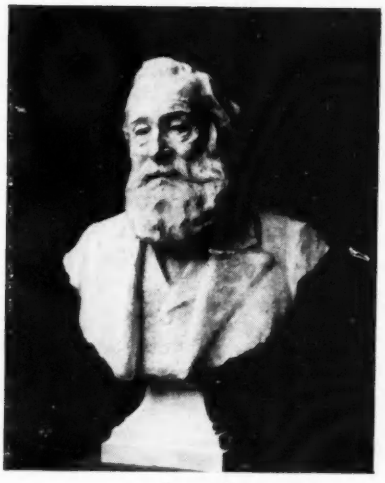

Figure 2
Bust of Perkin by Pomeroy

In the fall of the same year Perkin came to America to attend many meetings in his honor. These were held in New York, Boston, Washington and other cities. At the dinner in New York at Delmonico's on Oct 6, he was presented with the first "Perkin Medal," which has since been given annually to the American chemist who has "most distinguished himself by his services to applied chemistry."

The optimistic feeling of 50 years ago, in contrast to the fearfulness of today, was expressed in the words of Dr William Nichols on presenting the medal to Sir William:

> "You have seen the dawn of the golden age—the age of chemistry—that science which by synthesis will gather together the fragments and wastes of the other dynasties and build for the world a civilization which will last until the end."

All of these celebrations and words of praise in honor of one man make us wonder what this man was really like. How did he come to make his great discoveries? Why he instead of someone else?

Unfortunately there is a paucity of information about Perkin's early life. Not many scientists knew him well and there is little original written information.

It is amazing that a man whose work was so great has had no real biographer. The main primary sources of information concerning the man himself consist of a paper which Perkin wrote in 1886 on the origins of the coal tar industry in which he tells of his own early work and problems *(2);* the Perkin obituary notice which appeared in the *Journal of the Chemical Society* (London) (3), and finally the little mauve book, which we have already discussed.

From these limited sources we are able to put together a brief story. Perkin, the youngest son of George Perkin was born in London in 1838. Although his father wished him to become a builder and architect, young William became interested in chemistry. In spite of his father's opposition Perkin entered the Royal College of Science at the age of 15, listened to the chemical lectures of the great German chemist Hofmann, and finally in his 17th year was appointed to an assistantship under him. This latter work allowed Perkin no time for his own research and therefore the boy fixed up a laboratory in his home where he could try his own chemical experiments in the evenings.

Perkin's great discovery took place during the Easter vacation of 1856 when he was just 17 years old. Hofmann had previously made some remarks about the desirability of preparing quinine artificially. Perkin, basing his experiments on ideas which we know today to be unsound, first treated toluidine and then an aniline salt with bichromate of potash and obtained not quinine but a dirty dark precipitate from the latter.

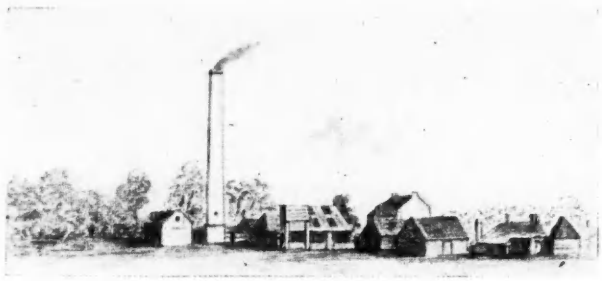

Figure 3
Greenford Green Works (1858)

It was the custom in those days for the organic chemist to be interested only in clear crystalline materials while dark tarry masses were always discarded as being worthless. Not so with Perkin. Some instinct caused him on this occasion to examine this dark mass. From this "useless" substance he isolated the first dye ever produced from coal tar——— mauve or aniline purple. It has been stated that, had Perkin experimented with pure aniline instead of with a rather crude material then available, his experiments would have been a failure and no valuable dye would have been discovered. This is not so; on the other hand it is true that magenta would not have been discovered, as it was several years later, had not the aniline used in the experiment been contaminated by toluidine.

Almost immediately Perkin sent a sample of his dye to a firm of dyers in Perth with the request that they try it on silk. Their report was "if your discovery does not make the goods too expensive, it is decidedly one of the most valuable that has come out for a long time. . . ."

While the first trials on cotton were unsuccessful (because no one realized the need for mordanting cotton), Perkin was not completely discouraged and he decided to patent the process for manufacturing the dye. It was not long before he had worked out methods for applying his mauve to cotton by means of mordants.

> "The nature of my invention consists in producing a new colouring matter for dyeing with a lilac or purple colour stuffs of silk, cotton, wool, and other materials in the manner following: I take a cold solution of sulphate of aniline, or a cold solution of sulphate of xylidine, or a cold solution of sulphate of cumidine, or a mixture of any one of such solutions with any others or other of them, and as much of a cold solution of a soluble bichromate as contains base enough to convert the sulphuric acid in any of the above-mentioned solutions into a neutral sulphate. I then mix the solutions and allow them to stand for 10 or 12 hours, when the mixture will consist of a black powder and a solution of a neutral sulphate. I then throw this mixture upon a very fine filter, and wash it with water till free from the neutral sulphate. I then dry the substance thus obtained at a temperature of 100° C, or 212° F, and digest it repeatedy with coal-tar naphtha, until it is free from a brown substance which is extracted by the naphtha. Any other substance than coal-tar naphtha may be used in which the brown substance is soluble and the coloring matter is not soluble. I then free the residue from the naphtha by evaporation, and digest it with methylated spirit, or any other liquid in which the coloring matter is soluble, which dissolves out the new coloring matter. I then separate the methylated spirit from the colouring matter by distillation, at a temperature of 100° C or 212° F." (4)

Surprisingly enough the father agreed to back his son with financial and other types of support. When Perkin and his father discussed the possibilities of manufacturing the dye with Hofmann, they met with discouragement but nevertheless father and son decided to go ahead with the venture. (Hofmann should not be condemned for his wrong advice for anyone using ordinary sound business judgment would certainly have discouraged the two from what appeared to be almost impossible. *Picture the team that was to found our modern organic chemical industry:* a young man of 17 with no factory or business experience and a limited chemical knowledge, together with a builder having no knowledge of chemistry or manufacturing whatsoever).

A building was commenced at Greenford Green in June, 1857. Perkin wrote years later . . . "at this time neither I nor my friends had seen the inside of a chemical works, and whatever knowledge I had was obtained from books. This, however, was not so serious a drawback as at first it might appear to be; as the kind of apparatus required and the character of the operation to be performed were so entirely different from any in use that there was little to copy from."

The many practical problems which Perkin and his associates had to overcome seem large in comparison with the actual discovery of the dye itself. Raw materials which were needed to manufacture the

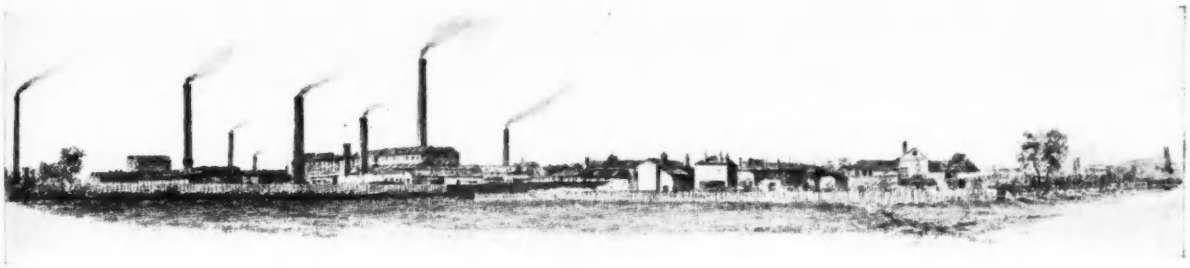

Figure 4
Greenford Green Works (1873)

dye were almost as scarce as rare elements. One of the first problems was to devise a method for making aniline from benzene. Even obtaining a satisfactory supply of benzene was in itself a problem. Perkin and his brother searched the whole country before they were able to obtain a reasonable supply of benzene for which they paid $1.25 per gallon. When they finally got this material into their factory it was so poor that it had to be redistilled.

Nitric acid of sufficient strength to convert benzene to nitrobenzene was not available and the Perkins had to manufacture their own, which in turn required the building of special apparatus.

Finally, the method of converting nitrobenzene to aniline had to be worked out by this 18-year-old boy and he had to devise the technique and the apparatus.

In spite of all the obstacles, within six months Perkin's mauve was being used in a British dyehouse and within a short time other concerns in England and France began its manufacture.

Over the next ten years Perkin continued his work on the manufacture and use of mauve and within a short time he had improved the method of dyeing this color on silk by using a soap bath and even had developed a process for its use in calico printing. At the same time Perkin's financial success surpassed all expectations.

In the year 1868 the synthesis of alizarin, the natural coloring matter of madder, had been worked out by Graebe and Liebermann, but their process was far too expensive to be of more than scientific interest. The starting material for their synthesis of alizarin was anthracene, a coal tar chemical with which Perkin had become familiar while studying with Hofmann. Graebe and Liebermann's work aroused Perkin's interest and in less than a year he had worked out a successful commercial process which soon made synthetic alizarin the prime red dye in place of madder. The same type of problems which confronted Perkin in obtaining benzene were even greater in the case of anthracene. Nevertheless by the end of 1869 Perkin's company had made a ton of alizarin and by 1871 they were making 220 tons per year.

In 1874 Perkin, who was then only 36, decided to retire from industry and to devote his life to pure research. The factory was sold and Perkin was able to face his future free from any money worries.

From thereon Perkin's work had little to do with dyestuffs. Researches on aldehydes and the synthesis of coumarin next held his attention. The synthesis of this latter product was the first step towards synthetic perfume or flavor. Finally Perkin spent his remaining years studying the magnetic rotation of organic compounds. This latter work — a difficult and important field of research from the theoretical viewpoint — has been considered by some scientists as Perkin's greatest.

Little is known about Perkin's personal life, which must have been quite uneventful, as he seemed to be uninterested in things outside of his own research. Perkin, married twice, had three sons and four daughters. His sons themselves were chemists in their own right. Perkin died on July 14, 1907, only a year after the 50th jubilee celebration of his great discovery.

An examination of the contemporary technical literature does raise some strange questions concerning Perkin's place in founding the great dye and coal-tar-chemical industries.

For example, the important book entitled "On Aniline and Its Derivatives" by the German chemist Reimann *(5)*, published 10 years after Perkin's discovery, certainly would not indicate to the casual reader Perkin's prime position in the development of the coal tar industry. The first dye discussed in this book is magenta, which was discovered by Hofmann, the teacher of Perkin and the person who most tried to discourage Perkin from trying to commercialize his mauve. Finally, in this authoritative source the only statement about Perkin's work which is given in a chapter on aniline blue and violet is as follows: . . . "a violet, the first of all aniline colors was discovered by Messrs Perkin and Church." The writer goes on to discuss in great detail the work of others without any additional word of appreciation for Perkin's great part. The question is: *Were the Germans, who had taken over the great work of Perkin, trying to build up their own role by giving main prominence to Hofmann, the German teacher, rather than to Perkin, the English student?*

Even Hofmann in his report on "Coloring Matters Derived from Coal Tars Shown at the French Exhibition, 1867," *(5)* makes only brief mention of his own student's part in the founding of this industry; yet at that time, 11 years after Perkin's discovery, Hofmann points out how a great industry had already arisen based on the chemicals from coal tar which not only has given us new colors but brought us also drugs, flavors and perfumes.

Finally, in William Crookes' monumental work "A Practical Handbook of Dyeing and Calico Printing," (London, 1874) *(6)*, nothing is mentioned about Perkin's place in the founding of the synthetic dye industry, yet a number of chapters are devoted to the synthetic dyestuffs, their use and even methods of application (developed by Perkin). Crookes was Hofmann's first assistant at the time Perkin came under Hofmann, and he must have known Perkin and the importance of his discovery. The question again is: *Was there a deliberate attempt to play down Perkin's importance? Could there have been jealousy on the part of the older Crookes? Or, did Perkin's inate modesty tend to keep down any favorable publicity?*

Another question which often arises is: *Why did England pay so little attention to the important discovery of their own Perkin and allow the Germans to take the lead in the dyestuff and organic chemical industries?* Perhaps no clear-cut answer can ever be found, but as one English writer puts his complaint . . . "Had the nation been far-seeing and wise, the industry would have flourished here (England) not merely for five or twenty years but permanently. Instead of this Hofmann returned to Germany in 1865, Caro in 1867, Martius about the year 1870, Witt in the year 1879. Perkin retired in 1874 and the band of great discoverers had dwindled to two or three." *(7)* Perhaps England's dominant place in the textile industry and its far-flung colonial possessions indicated no need for being concerned with the many things which

(Concluded on page 548)

● ABSTRACTS ●

A Simple Identification of Thermoplastic Fibers

J N Banks and P S Bembrick, *Textile J Australia* 28, 1522-3, February, 1954.

The term "thermoplastic fibers" has been used to group together those fibers which soften or melt when heated. Thermoplastic fibers belong to several chemical groups, and these fibers may be classified on the basis of chemical constitution as follows:

Polyamides

Nylon, Perlon L.

Vinyl Polymers

(a) Mainly vinyl chloride: Vinyon HH.

(b) Vinyl cyanide polymers: Orlon, Chemstrand.

(c) Vinyl chloride/cyanide polymers: Vinyon N, Dynel.

Vinylidene Chloride/Vinyl Chloride Copolymers

Saran, Velon, Fibrovyl, Tygan, Permalen.

Cellulose Acetate

Acetate.

Polyethylene

Courlene, Reevon.

Polyesters

Terylene, Dacron.

Fiber X-51, a copolymer of vinyl cyanide (acrylonitrile) and methyl methacrylate, and Perlon U (polyurethane), were not available for testing.

When attempting to identify unknown fibers it is usual to begin by burning samples of the fiber to observe the smell and type of ash produced. Thermoplastic fibers are indicated on burning by the production of a hard ash bead which cannot be crushed between the fingers.

The identification of members of this group is carried out by placing a small mass of fibers at the bottom of a 6" x ½" test tube, which is clamped in a horizontal position. A right-angle leading tube is inserted through a rubber stopper at the end of the test tube containing the sample, and a 6" x 1" test tube, containing 20 ml of distilled water and 3 drops of BHD Universal pH indicator, is clamped in such a manner that the end of the vertical arm of the leading tube is just below the surface of liquid in the test tube.

Heat is applied to the test tube containing the fibers, and is continued until the white fumes evolved have distilled into the indicator liquid. It is advisable to continue heating until the pyrolysis tube is emptied of fumes. The solution in the receiving tube is then stirred to produce a uniform color.

The colors produced by treating thermoplastic fibers in the foregoing manner are indicated in the following table, which also describes solubility tests used to complete the identification of the fiber.

Color of Solution

Blue: nylon, Orlon. In 90% phenol, soluble: nylon; insoluble: Orlon.

Red: Saran, Vinyon HH, Vinyon N, Dynel. In acetone, soluble (cold): Vinyon HH; soluble (at boil): Vinyon N, Dynel; insoluble: Saran.

Light Pink: acetate. In glacial acetic acid: soluble.

Yellow: Terylene, Dacron, Courlene. In boiling conc nitric acid, soluble: Terylene, Dacron; insoluble: Courlene.—WHC

The Dyeability of Modern Synthetics

J G Kern, *Dyestuffs* 40, 180-98, April, 1954.

The writer describes the inner structure of the modern synthetic "chemical" fibers, contrasting it with that of the natural fibers and those made from cellulose and the natural proteins.

From the point of view of dyeability, he says, a strict chemical classification is necessary. We must differentiate between those chemical fibers that contain aminogenic groups and others that are devoid of them.

Nylon 6, or Perlon L (caprolactam polymer) resembles wool in many of its dyeing properties. Due to a large number of amino sites and hydrogen bond linkages, it has excellent dyeability, the mechanism of dye fixation being quite similar to that of wool.

Nylon 66 (the ordinary type) differs from wool in that it has about one aminogenic group for thirty such groups in wool. In dyeing weak shades it has more affinity for acid dyes than wool, but as the dye concentration is increased, a saturation point is soon reached, beyond which only the wool absorbs the dye. The saturation point is influenced by the degree of orientation of the fiber and by the pH of the dyebath.

Those chemical fibers possessing no amino sites may be further divided into two classes: those containing no nitrogen (Dacron, Saran, and Vinyon), and those containing the monovalent nitrile radical (the polyacrylics, Orlon, Dynel, Acrilan, and X-51).

Dacron, which is somewhat similar to acetate in chemical structure, is dyed like acetate with disperse dyes. High temperatures, and the addition of suitable carriers, are essential for good dyeability. The same is true of Saran and Vinyon, except that these fibers, being thermoplastic at 110° C, may not be dyed above the boil. Ordinarily, acid dyes do not "take" on this group of fibers when dyed from aqueous solutions. "Dope" dyeing of Saran and Vinyon is suggested as a convenient way to produce fast shades with a larger variety of dyes.

First attempts to dye the polyacrylics were unusually discouraging. Disperse acetate and selected basic dyes could be used, but acid dyes could not be persuaded to color the fiber until the "cuprous ion" method was introduced. By this technique, it is now possible to use acid, direct, soluble leuco vat, metallized, and chrome dyes in complete color ranges.

Copolymerization of acrylonitrile with other monomers so as to produce amino sites on the fiber also gives it an affinity for acid dyes.

Polyethylene fibers consist wholly of hydrocarbon chains and cannot be colored by normal dyeing processes, but only by "dope" dyeing.—WHC

The Complementary Nature of Fibers from Natural and from Synthetic Polymers

J B Quig and R W Dennison, *Textile Research J* 24, 361-73, April, 1954.

The objective of this paper is to demonstrate the complementary nature of the natural fibers and the fibers made from synthetic polymers. Thus it is shown that the new fibers confer new properties and enhanced functional properties on the natural fibers and also on rayon and acetate; and, conversely, that the natural fibers and the man-made fibers, rayon and acetate, are adjunctive to the new fibers and likewise confer desirable properties on them.

There are evident advantages in choosing fibers that will best suit the use to which the final fabric will be put. By studying the ultimate usage of a fabric, the textile manufacturer can choose a single fiber or a blend of fibers from synthetic and natural materials that will render the most satisfactory service and have the desired aesthetic properties.

In this investigation, nylon staple, Dacron polyester staple, or Orlon acrylic staple was combined with rayon staple, acetate staple, or wool. Two component blends were made containing one of the new and one of the old fibers. The resulting blends of fibers were carefully pro-

(Continued on page 545)

Proceedings of the

American Association of Textile Chemists and Colorists

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Editor of Proceedings: Carl Z Draves, 30 Lahey St, New Hyde Park, N Y

AUGUST 16, 1954

AATCC CALENDAR

(A general calendar of events may be found page 548)

COUNCIL
1954—Sept 15, Nov 19.
1955—Jan 21, Apr 15, June 17

NATIONAL CONVENTIONS
Sept 15-18, 1954 (Atlanta Biltmore, Atlanta, Ga); Sept 21-23, 1955 (Chalfonte-Haddon Hall, Atlantic City, N J; 1956 (New York); 1957 (Boston).

NEW YORK SECTION
October 15, November 19 (Kohler's Swiss Chalet, Rochelle Park, N J); January 28 (Georgian Room, Hotel Statler, New York); February 25 (Skytop, Hotel Statler, New York); March 18, April 22, May 20 (Kohler's Swiss Chalet, Rochelle Park, N J).

NORTHERN NEW ENGLAND SECTION
Oct 8 (Colonial C C, Lynnfield, Mass); Dec 10 (Woodland Golf Club, Auburndale, Mass).

PACIFIC SOUTHWEST SECTION
Oct 30 (Outing—Ojai, Calif)

PIEDMONT SECTION
Oct 16 (Hotel Barringer, Charlotte, N C).

PHILADELPHIA SECTION
Sept 24, Oct 29 (Penn-Sherwood Hotel, Philadelphia, Pa); Dec 3 (Kugler's Restaurant, Philadelphia).

RHODE ISLAND SECTION
Oct 14 (Johnson's Dummocks Grille, Providence, R I); Dec 2 (Annual Meeting —Sheraton Biltmore, Providence, R I).

SOUTH CENTRAL SECTION
Dec 4 (Hotel Patten, Chattanooga).

SOUTHEASTERN SECTION
Dec 11 (Atlanta-Biltmore, Atlanta, Ga).

WESTERN NEW ENGLAND SECTION
Oct 1, Nov 12, Dec 10 (Rapp's Restaurant, Shelton, Conn).

WESTERN NEW YORK SECTION
Oct 8 (Buffalo, N Y); Nov 27 (Hamilton, Ont); Jan 14 (Buffalo); Mar 4 (Hamilton, Ont); April 22 (Buffalo); June 24 (Outing)

NOTICE TO SECRETARIES AND PUBLICITY CHAIRMEN OF LOCAL SECTIONS

Papers presented before local sections should be sent to Dr Carl Z Draves, Editor of the *Proceedings*, 30 Lahey Street, New Hyde Park, New York. Authors should provide two copies for this purpose.

Reports of local section meetings should be sent to the American Dyestuff Reporter with copies going to Dr H C Chapin, National Secretary.

Dates of meetings and advance notices of meetings should be sent to the American Dyestuff Reporter with copies also going to Dr Chapin. For publication in any particular issue, information should be in the office of the Reporter 17 days before the issuance date.

AATCC Monograph No. 2
"THE APPLICATION OF VAT DYES"

"The group of fifteen editors responsible for this monograph consists of a well-balanced cross-section of American industry concerned with the production, marketing and application of vat dyes. The AATCC is to be congratulated on the production of a comprehensive survey of American vat dyeing and printing practice which is the major theme of this application . . . the book will be useful as a work of reference at this side of the Atlantic and as a working manual for the American colorists for whom it was designed. . . . If a clear account of American practice is required . . . the enquirer *must* have access to this volume."—*JOURNAL OF THE TEXTILE INSTITUTE* (England).

"This book . . . is abreast of the latest technical developments and research. Its value is increased because of the lack of books in this field today . . . we can readily recommend this book to all technical and practical men"—*MELLIAND TEXTILBERICHTE* (Germany).

"This monograph contains the work of many mill-experienced authors, plus good, sound chemical and application principles developed in the laboratories and mills enjoying AATCC membership. . . . This book puts between two covers much information that a dyer is constantly searching for. It is a good investment for any laboratory, dyehouse, or printshop."—*TEXTILE WORLD.*

". . . this monograph should be in the hands of every user of vat dyestuffs, every student and every teacher. The book is well indexed and includes valuable lists of equivalent trade names. It will certainly take its place as a standard book of reference."—*JOURNAL OF THE SOCIETY OF DYERS AND COLOURISTS* (England).

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1954 National Convention and "The South's First Textile Wet Processing Exhibit"——

SPONSORED BY THE SOUTHERN REGION ★ THE ATLANTA BILTMORE ★ ATLANTA, GEORGIA ★ SEPTEMBER 15, 16, 17, 18

LADIES COMMITTEE TO FEATURE DIVERSIFIED PROGRAM AT ATLANTA

WILLIAM B GRIFFIN, chairman of the Ladies Committee for the 1954 Convention, reports that plans are well under way to extend the visiting ladies a cordial welcome and to make their visit to Atlanta an occasion to be remembered with much pleasure.

Room #10 on the Atlanta Biltmore Hotel's Mezzanine has been reserved as Ladies Headquarters, and members of the Committee will be present at all times to welcome visitors, furnish information and make every effort to make milady's stay more pleasant while the Convention is in progress. All visiting ladies are urged to use Room #10 for a bridge game or a friendly visit any time they have free time.

In addition to the sightseeing tours on Friday and the football buffet luncheon, football game and Annual Banquet on Saturday, all functions to which all registered ladies are welcome and urged to attend, the Ladies Committee has planned the following special events, which are complimentary for lady registrants:

Wednesday, Sept 15

5:30-6:00 pm ——— LADIES WELCOME PARTY ——— *Pompeian Room, Atlanta Biltmore Hotel*———This party is designed to get the visiting ladies off to a good start in renewing old friendships and making new friends.

Thursday, Sept 16

12:30 pm ——— LUNCHEON ——— HONORING OFFICERS' WIVES———*Capital City Country Club* ——— This luncheon will include a program on "Color and the Woman". The Ladies of the Committee are planning to make this a most enjoyable and informative affair. Transportation to and from the country club will be complimentary and special busses will be provided.

Friday, Sept 17

10:30 am ——— COFFEE ——— Tea Room, Rich's, Inc.

LADIES COMMITTEE—1954 AATCC CONVENTION—ATLANTA, GA

Seated (l to r): **Mrs George L Dozier, Mrs William B Griffin, Mrs C Russell Gill, Mrs T Howard McCamy, Mrs W A Haines, Mrs T Max Ferguson**

Standing (l to r): **Mrs James W Swiney, Mrs Francis S Webster, Jr, Mrs Paul G Wear, Mrs Edward R Ravenel, Paul G Wear (assistant general chairman of the 1954 Convention), Mrs Paul V Seydel, William B Griffin (chairman, Ladies Committee), Mrs David Meriwether, T Max Ferguson (assistant chairman, Ladies Committee), Mrs John K Boykin**

Other members of the Committee who were not present at the time photo was taken: Mrs Paul O Anderson, Mrs John C Cook, Mrs Samuel L Hayes, Mrs Milton Harris, Mrs A Kempton Haynes, Mrs Curt Mueller, Mrs C Norris Rabold, Mrs Henry A Rutherford, Mrs Thomas R Smith, Mrs H Gillespie Smith, Mrs Laurie E Whittelsey

William B Griffin

Chairman, Ladies Committee

Mr Griffin, who has served the Southeastern Section both as secretary and councilor, has been with the Dexter Chemical Corporation since 1952 as a district representative in Georgia, Alabama and Tennessee

Walter M Scott

Chairman, Technical Program

Dr Scott, a councilor for the Washington Section, is assistant director of utilization research, Bureau of Agriculture and Industrial Chemistry, U S Department of Agriculture, Washington, D C

TECHNICAL PROGRAM

Under the chairmanship of Walter M Scott, the Technical Program for the Atlanta Convention will be comprised of five symposiums featuring twenty-three papers, which will be presented as follows:

Wednesday, Sept 15

2:00 pm—SYMPOSIUM—"PREPARATION AND DYEING OF TEXTILES"—Walter M Scott, presiding

"Desizing Procedures in Relation to Enzyme Evaluation"—H C Borghetty, Rohm & Haas Co

"Sources of Color in Cotton"—S A Simon and Carlyle Harmon, Chicopee Mfg Corp

"Some Notes on the Technology of the Single-Stage Continuous Bleaching Process"—T E Bell, H D Terhune, and M H Rowe, E I duPont de Nemours & Co, Inc

"Spun Colored Fibers"—Geoffrey V Lund, Courtaulds, Ltd

"A Progress Report on the Bond Processing Machine"—Karl Ruppenthal, Pittsburgh Coke & Chemical Co

Thursday, Sept 16

9:00 am—SYMPOSIUM—"DYEING OF TEXTILES"—Kenneth S Campbell, presiding

"The Influence of Temperature on Vat Dye Application"—M R Fox, Imperial Chemical Industries, Ltd

"A Study of Carriers in Dyeing Dacron Polyester Fiber"—C L Zimmerman, J M Mecco, and A J Carlino, American Cyanamid Co

"Acrilan Dyeing"—W H Hindle, Chemstrand Corp

2:30 pm—SYMPOSIUM—"FINISHING OF TEXTILES"—Leonard Smith, presiding

"Application of THPC Flame-Retardant Process to Cotton Fabrics"—J D Guthrie and W A Reeves, Southern Utilization Research Branch, U S Dept of Agriculture

"Wrinkle-Resistant Treatment of Cotton"—T F Cooke, American Cyanamid Co

"Nitrile Latices—A New Concept in Textile Finishing"—N H Sherwood, B F Goodrich Chemical Co

"Antistatic Action vs Molecular Structure"—G R Ward, General Aniline & Film Corp

"Finishing of Fabrics from Synthetic Fibers"—J H Andreen, E I du Pont de Nemours & Co, Inc

Friday, Sept 17

9:00 am—SYMPOSIUM—"PRINTING OF TEXTILES"—Raphael E Rupp, presiding

"Fast Color Printing"—Raymond W Jacoby, Ciba Co, Inc

"New Printing Developments with Vat Colors"—A K Saville, E I duPont de Nemours & Co, Inc

"The Use of Resins in Producing Colored Three-Dimensional Styles on Cotton Fabrics"—R H Phillips and E W Lawrence, Cranston Print Works

"Printing and Related Operations on Glass Decorative Fabrics"—R F Caroselli, Owens Corning Fiberglas Corp

9:00 am—SYMPOSIUM—"WASTE DISPOSAL PROBLEMS OF SOUTHERN MILLS"—R Hobart Souther, presiding

"Relation of Federal Stream Pollution Laws to Industry"—Lewis A Young, U S Public Health Service

"Treatment of Sulfur, Vat and Other Dye Wastes with Carbon Dioxide and Flue Gases"—H R Murdock, Harold R Murdock Associates

"Cotton Slashing with Synthetic Compounds as a Means toward Pollution Abatement"—Duane Snyder, Crompton-Shenandoah Co

"Bleachery and Dyehouse Waste Studies"—John L Brown, Jr, Cannon Mills Co

"Studies on Textile Waste Disposal"—D F Smallhorst, Texas State Dept of Health

"Treatment of Textile Mill Waste and Domestic Sewage"—T A Alspaugh, Cone Mills

* * * * * * * *

Panelists at the latter symposium will be W R Steele, Semet-Solvay Division, Allied Chemical & Dye Corp; W H Weir, Georgia State Dept of Health: E C Hubbard, N C Stream Sanitation Committee; George A Rhame, South Carolina State Board of Health; Percival Theel, Philadelphia Textile Institute; and E A Leonard, National Technical Task Committee on Industrial Wastes.

SPECIAL TRAIN TO ATLANTA

THROUGH the cooperation of Wyss Barker, chairman of the transportation committee, arrangements have been made with the Southern Railway for a special train to the Atlanta Convention. The train will consist of roomettes, bedrooms, and all compartment-drawing room cars, a lounge car and observation car. The dining cars will feature souvenir menus for the AATCC. The schedule for the train is as follows:

Going—September 14		*Returning—September 19*	
1:50 pm EST	—Lv New York	1:00 pm EST	—Lv Atlanta
2:05 pm	—Lv Newark	3:30 am	—Ar Washington*
3:35 pm	—Lv Phila (30th St)	4:51 am	—Ar Baltimore
4:08 pm	—Lv Wilmington	5:51 am	—Ar Wilmington
5:10 pm	—Lv Baltimore	6:22 am	—Ar Philadelphia
6:10 pm	—Lv Washington	7:54 am	—Ar Newark
8:00 am EST	—Ar Atlanta	8:10 am EST	—Ar New York

* If there are sufficient passengers from Washington, an extra car will be cut out of train and parked at Washington for occupancy until 7:30 am EST.

The one-way and round trip rail rates and one-way Pullman rates are as follows, including the 10% tax:

From	*One-way RR Fare*	*Round-trip RR Fare*	*Roomette*	*Bedrm for 1*	*Bedrm for 2*	*Compt for 2*	*Drawing Rm for 2 Or 3*
New York	$38.17	$70.95	$14.85	$20.08	$23.21	$29.98	$40.15
Newark	37.77	70.16	14.85	20.08	23.21	29.98	40.15
Philadelphia	33.73	62.06	13.20	18.04	20.90	27.06	36.08
Wilmington	32.48	59.58	13.20	18.04	20.90	27.06	36.08
Baltimore	29.02	52.65	11.66	15.90	18.37	23.27	31.79
Washington	27.12	48.84	11.66	15.90	18.37	23.27	31.79

Reservations may be made with the following representatives:

Boston 16, Mass—L G Sak, N E Passenger Agent, 80 Boylston St

Philadelphia, Pa—W M McCullough, Asst Gen Pass Agent, 1408 Western Saving Fund Bldg

Baltimore 2, Md—E B Howes, District Pass Agent, 1750 Mathieson Bldg

Washington 13, D C—N B Ballinger, Asst Gen Pass Agent, 15th & K Streets, N W

New York 36, N Y—P A Schumpert, Gen Pass Agent, 500 Fifth Ave

It is urged that you make your reservations at once, in order to assure sufficient patronage for the special train.

ONE HUNDRED AND NINETY-SECOND COUNCIL MEETING

THE Council held its 192nd meeting in the Hotel New Yorker, New York, N Y, on Tuesday morning, June 15, 1954. Present were President J Robert Bonnar, *presiding;* George L Baxter, Samuel L Hayes and George O Linberg, *vice presidents;* Albert E Sampson, *treasurer;* Charles W Dorn, *vice chairman of the Executive Committee on Research;* Carl Z Draves and P J Wood, *past presidents;* Elmer E Fickett, John P Ploubides, Robert D Robinson and Sawyer F Sylvester, representing Northern New England; Raymond W Jacoby, representing Rhode Island; Raymond J Carey, representing Western New England; Robert C Allison, Matthew J Babey, Herman E Hager, John H Hennessey, Patrick J Kennedy, Paul J Luck and James J Marshall, representing New York; Carleton T Anderson, Harry L Morgan, Thomas R Scanlan, Jr, Percival Theel and Frederick V Traut, representing Philadelphia; J Edward Lynn representing Western New York; Walter M Scott representing Washington; S Jack Davis, representing Southeast; Joseph D Mosheim representing South Central; Kenneth H Barnard of the Committee on Conventions; William A Holst of the Committee on Constitution and Bylaws; Glenn D Jackson, Jr of the Publicity Committee; Ernest R Kaswell, chairman of the Northern New England Section; and Harold C Chapin and Richard R Frey of the secretary's office.

The secretary's report of the 191st Council meeting and financial report of May 20th, and the treasurer's report of May 24th, were accepted. The budget prepared by the Appropriations Committee for the year beginning August 1, 1954 was approved.

Reporting for the Executive Committee on Research, Mr Dorn again emphasized the policy of the Association to offer its tests freely to all who would use them, but not to sponsor legislation involving them. The Committee did not favor change in the Association's flammability test until supported by further experimental evidence. More information on the interpretation of tests would be incomporated in the *1954 Year Book.* Further progress on the Quartermaster-Air Force Dye Survey was reported by Mr Holst. An invitation was received from the Textile Technical Federation of Canada to its Seminar of September 9 to 11 in Queen's University, Kingston, Ontario.

Professor Theel presented the recently completed Bibliography of Textile Waste Studies, to be published in the *American Dyestuff Reporter.* Mr Holst was made a member of the Publications Committee, and chairman of a committee, with Mr Bonnar and Mr Jacoby also members, to advise Mr Cady on revision of dyestuff listing for the *1955 Year Book.* Both old and new *Colour Index* numbers would be listed, making this volume a permanent reference for the transition. Listing of dyes made in this country will be confined, as in the *Colour Index,* to products of companies listed as manufacturers of dyes in the publication entitled "Synthetic Organic Chemicals" issued by the U S Tariff Commission, except for a company which is the sole agent of a manufacturer so listed. On the *1954 Year Book* wrappers will be printed notes of significant changes in test methods since publication of the 1953 volume.

Mr Barnard reported nearly all space taken for exhibits at the Atlanta convention. Dr Scott discussed the technical program. For the Perkin Centennial of 1956 Mr Jacoby reported a program of 22 topics accepted for special coverage by 26 associations, other than our own.

Mr Holst reported proofs for the *Colour Index* still coming in and available for inspection in the offices of the *American Dyestuff Reporter.* Mr Sampson had word from England that publication might be as early as November, 1955. He invited inspection of sample bindings from English and American sources.

For the Committee on Membership and Local Sections Mr Hayes reported organization of the Western New York Section, with setting of boundaries to be deferred pending investigation of member preferences. Dr Lynn reported on the first meeting of the Section and election of officers. New bylaws of the Georgia Institute of Technology Student Chapter were approved. Each of the following was elected to the class of membership indicated:

CORPORATE

Aldon Rug Mills, Inc
Peerless Color Company, Inc
Textile World

SENIOR

A P Baker
H A Briggs
F Brody
H P Brokaw
G C Campari
G H Campbell
W M Carr
U F Finaly
W A Fisher
S Foster
P E Gerold
R A Gilliam
J B Gregory
F A Hawkins
S Heilveil
H F Holmes
S Inoue
H L Jones, Jr
W R Joyner
A G Koos
R S Lembeck
E E Martin
C S McCrorey
I Moskowitz
G A Palamara
R J Pavlin
E A Pendzick
N E Perra
A W Perregrino
M C Plummer
S J Prant
E G Reep
R A Pearson
M D Rufty
W M Smith
S S Spielman
J E Stahl
F M Stevenson
V D Stibolt
A T Thorne
F J Tuohey
J L Walsh
W H White

(Concluded on page P540)

SECRETARY'S FINANCIAL REPORT—MAY 20, 1954

	Applications	Dues Regular & Reinstate	Dues Corporate & Sustaining	Miscellaneous	Totals
Received & transmitted to Treasurer August 1, 1953 to March 31, 1954	3389.00	45022.25	46482.50	24332.77	119226.52
March 31 to May 20, 1954	593.00	418.00	660.00	2344.89*	4015.89
Total in fiscal year to May 20	3982.00	45440.25	47142.50	26677.66	123242.41
Leaving deposited by Treasurer with Secretary,					9124.51
For comparison, receipts to May 19, 1953	4357.50	44111.50	47917.50	13215.48	109601.98

* Miscellaneous items,

Dividend,	11.25
Reporters and reprints,	15.30
Book resold,	1.10
Dry cleaning kit,	1.00
Year Books,	312.42
Crockmeters,	619.74
Crock cloth,	85.95
Multifiber cloth,	429.22
Moth cloth,	42.50
Water test apparatus,	18.10
Dyed standards,	72.00
Knitted tubing,	10.00
Gas fading units,	79.00
Buttons,	7.50
Color transfer charts,	132.50
Analytical Methods,	53.00
Application of Vat Dyes	340.15
Standard grease wool,	53.25
Cotton skeins,	36.81
Grey scales,	13.50
Liners for Acceleroter,	10.60
	2344.89

1953 Intersectional Contest——

INVESTIGATION OF SODIUM SULFOXYLATE-FORMALDEHYE AS THE PRIMARY REDUCING AGENT IN VAT DYEING*

SOUTH CENTRAL SECTION

COMMITTEE

Robert D Blum, Jr, *Chairman*
May Hosiery Mills

William F Luther
Dixie Mercerizing Co

Wilbur K Newman
Peerless Woolen Mills

Charles A Spratt
National Aniline Div
Allied Chem & Dye Corp

H A Webb
General Dyestuff Co

Charles O Starnes
American Aniline Products, Inc

J C Whitt
Standard-Coosa-Thatcher Co

Walter K Mobley
Central Franklin Process Co

Donald Grunther
Burkart-Schier Chem Co

The objective of this study was to determine the possibilities of the utilization of formaldehydesulfoxylate, both with and without hydrosulfite, in obtaining advantages in dyeing and to evaluate sulfoxylate dyeing with some vat dyestuffs in practical application.

Determinations were made of the reduction potentials of sulfoxylate under dyeing conditions. At temperatures above 150°F these become comparable with those of the usual alkaline hydrosulfite baths employed below 150°F in the old conventional vat-dyeing methods.

Laboratory procedures were worked out, which permitted production-scale batch dyeings at liquor ratios of 8:1 and 20:1. It is important in the use of sulfoxylate either alone in alkaline solution or in combination with hydrosulfite in alkaline solution that the optimum conditions for attaining penetration, levelness, and exhaustion be determined.

Besides giving dyeings of fully equal shade, strength and fastness, the use of sulfoxylate in dyeing offers the following advantages:

1) Easier and better control of exhaustion rate.

2) Low "strike".

3) Increased leuco stability at high temperatures, particularly with halogenated indanthrones.

4) Increased stability of reducing agent.

INTRODUCTION

IN the application of vat dyestuffs, particularly in batch-type operations such as package dyeing, the rapid exhaustion rate of many vat dyes has always been considered a basic problem. *(1)*, The exhaustion rate. *(2)*, together with the rate of diffusion, are generally regarded as critical factors in the attainment of levelness, a broad term which we interpret as including penetration and even distribution of dyestuff throughout all portions of the mass of fiber, yarn, or fabric to be dyed. Retarding agents are a useful aid in the control of exhaustion rate, and the temperature-gradient method can be used with some dyes. Both methods are used with success but are not without disadvantages, which are well known *(1)*. Specific references were not found in the literature to the use of a weak reducing agent to effect a very slow, or loosely termed "partial," reduction of vat dyestuffs, prior to the addition of sodium hydrosulfite for the purpose of attaining a slow initial reduction and exhaustion. However, an early application of this principle was the use of sugars and dextrines. Later the practice of using a small quantity of sodium sulfoxylateformaldehyde (hereafter referred to as "sulfoxylate") for the same purpose was carried out with a greater degree of success, apparently because of its greater stability in hot alkaline solution. The practice is widely used in the vat dyeing of seamless cotton hosiery. It was observed in this dyeing operation that the exhaustion rate was initially slowed, and that the degree of reduction and rate of initial exhaustion in the sulfoxylate dyebaths varied considerably with individual dyestuffs.

Although the use of sulfoxylate as the reducing agent in printing is well known, and many special but limited applications in vat dyeing have been reported *(4, 5, 6, 15, 19, 20 and 22)*, the literature did not reveal a thorough study of the general possibilities of sulfoxylate as a primary reducing agent in the broad field of vat dyeing. Further, though the reduction potentials of sulfoxylate had been briefly reported *(7)*, this investigation was not complete enough to indicate the possibilities of its use in normal dyeing concentrations. The first step, therefore, in a consideration of the practicality and possible value of the investigation which we contemplated was a comparison between redox potentials of sulfoxylate with those developed with hydrosulfite, which will hereafter be called "hydro."

Upon measuring the reduction potentials of sulfoxylate-sodium hydroxide baths, it was found that the reduction potentials developed were comparable to those in which hydro was used as the reducing agent. This finding led to preliminary dyeings in which sulfoxylate was used without hydro, and which showed that many dyestuffs could be satisfactorily dyed with sulfoxylate as the reducing agent. These dyeings indicated that improved dyeings in many applications might be obtained by eliminating hydro from the system. It was then decided that the objectives of the investigation were to be as follows:

1) To determine whether the use of sulfoxylate offers advantages in dyeing, either in conjunction with hydro or without hydro.

2) To evaluate the sulfoxylate reduction of some vat dyestuffs and applications thereof in dyeing operations.

EXPERIMENTAL

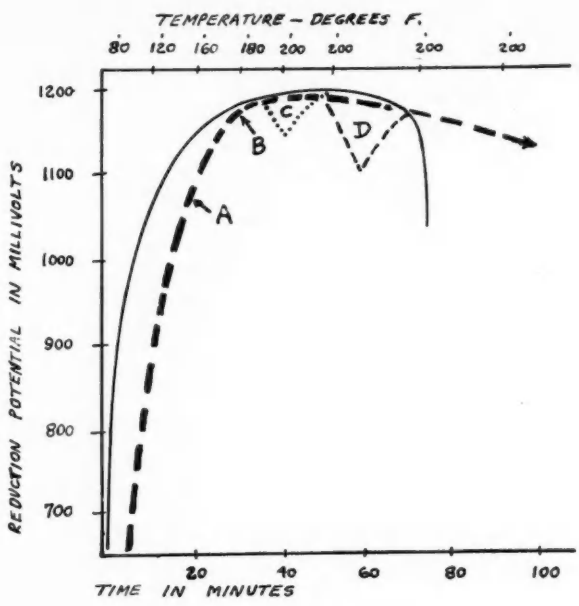
APPARATUS———A portable Foxboro Dynalog Redox Recorder, with interchangeable-range units of 200-1200 millivolts and 800-1400 millivolts, was used in all experiments. Laboratory yarn dyeing on 1⅝" tubes was carried out in a one-pound Gaston County package dyeing machine, equipped with jacketed dyeing kier for heating and cooling indirectly; bath ratio was approximately 10:1 on all packages dyed. This moderately long liquor ratio was necessary to keep the bath in the expansion tank at a high enough level to cover the electrodes. Knit goods and woven piece goods were dyed at a 20:1 bath ratio in stainless-steel beakers with temperature controlled by

* Presented by Robert D Blum, Jr, at Chicago, Ill on Sept 19, 1953. Submitted to *Am Dyestuff Reptr* by the Editor of Proceedings on June 9, 1954.

water baths. In production dyeings, yarn was dyed on 1⅝" tubes at an 8:1 bath ratio in a Gaston County 500-pound package dyeing machine, equipped with steam coils and cooling coils. Knit goods were dyed at a 20:1 bath ratio in both open-top paddle machines and in closed rotary machines.

High-temperature (over 210°F) dyeings at 8:1 bath ratios were run in the Gaston County Laboratory Package Dyeing Machine. Those at very low bath ratios were carried out in laboratory Pyrex U-tube dyeing vessels in which both hot oil and mercury were used. The Macbeth Model "A" Laboratory pH Meter was used for pH determinations. It was impossible to obtain the redox potentials on these dyeings because of mechanical difficulties in immersing the electrodes.

REDUCTION POTENTIALS——In order to check the reduction potentials obtained, experimentally determined reduction potentials on blank vats with hydro from General Dyestuff Corporation were compared (Table I) with those we obtained. It is to be noted that a substantial loss in potential was effected by previously dissolving the hydro in a NaOH solution as compared with adding the hydro dry to the diluted NaOH solution of the dyebath. This was also found to be true with sulfoxylate in Table I, in which reduction potentials of sulfoxylate-NaOH blank vats were determined. It is to be noted further that this loss of potential is not merely an initial loss but is reflected in the stabilized potential at high temperatures, as verified in readings taken during dyeing.



——— Hydro-NaOH—1 oz/gal
- - - - Sulfoxylate-NaOH—1 oz/gal

Rate of temperature rise is constant for both curves, approx 30 min rise from 80 to 200° F, or 4° per min.

Composite curve based on experience with anthraquinone dyes.
A—Initial leuco formation. B—Complete leuco formation.
Effect of cooling and reheating: C—Hydro. D—Sulfoxylate.

REDOX POTENTIALS VS TIME

Figure 1
Hydro dyeings compared with sulfoxylate

In Table II, in which a tabulation of reduction potentials of sulfoxylate-NaOH system is made, it is seen that, with practical concentrations of sulfoxylate, reduction potentials well beyond the apparent desired range for leuco potentials of the vat dyestuffs, can be obtained. It is also to be noted that the potentials of baths of comparatively low alkalinity offer the

TABLE I
AVERAGE REDUCTION POTENTIAL VALUES IN MILLIVOLTS — SODIUM HYDROSULFITE

NaOH and Hydro oz/gal	*90° F*			*120° F*			*150° F*			*180° F*			*200° F*		
	A	*G*	*B*	*A*	*G*	*B*	*A*	*G*	*B*	*A*	*G*	*B*	*A*	*G*	*B*
0.5	865	810	980	890	880	1045	920	920	1090	960	960	1100	1015	1020	1125
1.5	925	850	835	910	910	1080	950	950	1155	980	1000	1170	1050	1090	1185
2.5	930	885	785	940	930	1090	960	990	1180	1050	1050	1230	1090	1120	1220

A—Hydro previously dissolved in caustic soda solution
G—Values furnished by General Dyestuff Corporation
B—Dry hydro added to diluted caustic soda dyebath

TABLE II
AVERAGE REDUCTION POTENTIALS IN MILLIVOLTS — SODIUM SULFOXYLATEFORMALDEHYDE

NaOH *oz/gal*	*SSF*	*90° F*	*100° F*	*110° F*	*120° F*	*130° F*	*140° F*	*150° F*	*160° F*	*170° F*	*180° F*	*190° F*	*200° F*
1.00	1.00	630	695	830	850	885	950	1050	1145	1175	1200	1230	1240
					(700)	(735)	(780)	(860)	(900)	(915)	(940)	(965)	(990)
0.75	0.75	630	670	815	840	895	940	1045	1100	1155	1170	1180	1215
0.50	0.50	600	630	705	785	850	900	980	1075	1100	1140	1155	1180
					(580)	(660)	(705)	(770)	(835)	(900)	(960)	(970)	(980)
0.125	0.75	535	580	725	800	835	855	880	940	950	975	1120	1145

(Figures in parenthesis indicate sulfoxylate previously dissolved in NaOH solution)

TABLE III
EVALUATIONS OF LABORATORY DYEINGS ON COTTON WITH SULFOXYLATE AT 20:1

Colour Index	Dyestuff	Depth Adaptability Lt	Med	Hvy	Hvy (H)	Conditions Alk Temp F	Comparisons with Hydro Controls Value	Quality	Shade	Apparent Appln
Pr 9	Anth Vat Yellow GC	G	F	F	G	Mod 160-200	W	C	C	N-SE
—	Anth Vat Yellow PGA	G	G	F	G	Mod 150-180	C	C	C	N-SE
—	Anth Vat Fast Yellow	G	G	X	X	Mod 140-180	C	C	C	HTS
1118	Anth Vat Yellow G	G	G	F	G	Low 140-180	Wsl	C	C	N-SE
1098	Anth Vat Orange RRT	G	F	F	G	Mod 160-200	Wsl	C	C	HTS
1217	Indigoid Vat Orange R	G	G	G	X	Low 140-200	C	C	C	Gen
—	Calcosol Flaming 2R	G	G	X	X	Mod 140-190	Wsl	C	C	HTS
—	Algol Orange RG	G	G	X	X	Low 140-200	C	B	C	Gen-SE
—	Calcosol Gl Orange 6RD	G	G	X	X	Mod 140-190	Wsl	C	C	HTS
Pr 106	Indigoid Vat Scarlet 2B	G	G	G	X	Low 140-200	B	B	C	Gen
Pr 107	Indigoid Vat Scarlet 2G	G	G	G	X	Low 140-200	B	B	C	Gen
1162	Anth Vat Red BN	G	F	F	G	Low 140-200	W	C	C	N
Pr 109	Indigoid Vat Pink FF	G	G	G	X	Mod 140-200	B	B	C	Gen (a)
Pr 296	Anth Vat Red FBB	G	G	X	X	Mod 160-200	C	C	C	SE (b)
1212	Indigoid Vat Red 3B	G	G	X	X	Low 140-200	Wsl	C	R	N
1135	Anth Vat Brill Violet RKN	G	G	X	X	Mod 160-200	C	C	C	HTS
1104	Anth Vat Brill Violet 4RN	G	G	G	G	Mod 160-200	C	B	C	Gen (c)
Pr 288	Anth Vat Brill Violet 3BA	G	G	X	X	Mod 160-200	Wsl	B	C	LS
1099	Anth Fat Dark Blue BO	G	G	G	X	V Hi 160-200	B	B	G	Gen (d)
1100	Anth Vat Navy Blue RT	G	G	F	G	Hi 160-200	C	C	C	Gen
—	Ponsol Navy Blue	X	X	G	X	Mod. 160-200	B	B	C	Gen
1184	Indigoid Vat Blue 4B	G	G	P	G	V Low 140-200	C	B	C	Gen (a)
—	Indanthrene Brill Blue 4G	G	F	F	F	Low 140-180	W	C	C	LS
969	Hydron Blue	X	G	G	G	Low 140-200	B	B	C	Gen (a) (e)
1106	Anth Vat Blue RS	G	G	G	G	High 130-180	B	B	B	Gen HTS
1112	Anth Vat Blue GCD	G	G	G	G	High 130-180	B	B	B	Gen HTS
1113	Anth Vat Blue BF	G	G	G	G	V Hi 130-180	B	B	B	Gen HTS
—	Indan Brill Blue RCL	G	G	F	G	High 130-200	C	B	C	Gen HTS
—	Indan Brill Blue CLN	G	G	X	X	Mod 140-200	C	C	C	N
—	Anth Vat Blue-Green Y	G	G	F	G	High 150-180	C	B	C	Gen SE
1101	Anth Vat Jade Green	G	G	G	G	High 150-160	Wsl	C	C	Gen SE
—	Ahcovat Brill Green 7G	G	G	X	X	Mod 150-180	C	C	C	LS
Pr 293	Anth Vat Olive Green B	G	G	X	X	Mod 150-200	C	B	C	SE (f)
1150	Anth Vat Olive R	F	F	X	X	High 170-200	W	C	R	SE
Pr 122	Anth Vat Khaki 2G	P	P	P	G	V Hi 170-205	W	B	C	HTS
1152	Anth Vat Brown G	G	F	X	X	Mod 160-200	W	B	C	LS
1151	Anth Vat Brown R	G	G	P	G	Low 160-200	Wsl	B	C	LS
Pr 121	Indigoid Vat Brown G	G	G	F	G	Low 160-200	Wsl	B	C	LS
Pr 118	Anth Vat Brown BR	G	F	F	G	Mod 160-200	Wsl	C	C	LS
—	Mayvat Brown UF	G	F	P	G	High 160-200	Wsl	B	C	Gen
—	Ahcovat Brown DRM	G	F	P	G	High 160-200	Wsl	B	C	Gen
—	Ahcovat Brown 6R	G	G	F	G	Mod 160-200	Wsl	B	C	SE
—	Calcosol Vat Copper Br	G	F	F	G	Mod 160-200	Wsl	C	C	HTS
—	Mayvat Grey 2RT	G	G	X	X	Mod 160-200	C	B	C	LS
—	Calcosol Gray BD	G	G	X	X	Mod 160-200	C	B	C	LS
—	Indanthrene Gray GNF	G	G	X	X	Mod 160-200	C	B	C	LS
—	Ponsol Gray R	G	G	X	X	Mod 160-200	C	B	G	LS
—	Ponsol Dir Black 3G	X	G	F	G	Mod 160-200	C	C	C	Gen
1102	Anth Vat Black BBD	X	G	G	G	High 170-205	C	C	R	Gen (g)

ABBREVIATIONS AND NOTES TO TABLE III

Hvy-(H)—Indicates 2 to 5% Hydrosulfite added for last 5-10 minutes of dyeing cycle.
Low Alkalinity (Alk)—Indicates 5-7% NaOH. Very low (V)—less than 5% usually with Na_2CO_3 as buffering agent.
G—Good F—Fair P—Poor X—Not run or insufficient client data.
Moderate (Mod) alkalinity indicates 8-20% NaOH. High Alkalinity indicates 20-30% NaOH. Very (V) high indicates over 30% NaOH.
Quantity of sulfoxylate varied from 8 to 20%. First temperature indicates approximate point of initial leuco formation; second temperature is final dyeing temperature. Total dyeing time averaged 35-45 minutes.
C—Comparable B—Better W—Weaker R—Redder G—Green Wsl—Slightly weaker.
SE—Only where slower exhaustion would be advantageous.
HTS—Only where improved high temperature stability is desired.
LS—Recommended for light shades.
Gen—General application indicated.
N—No obvious application.
(a) Salt required for optimum color value.
(b) Rate of exhaustion very sensitive to temperature increases.
(c) Redder shade at low alkalinity.
(d) Greener and more desirable shade than control.
(e) Cleaner dyeings.
(f) Shade much brighter than control with very low alkalinity.
(g) Did not require chlorination for reddish black shade.

possibility of better utilizing certain dyestuffs, the leucos of which are known to be sensitive or unstable to excess alkalinity.

In reply to a request for available leuco potentials for individual vat dyestuffs, Donald E Marnon of General Dyestuff Corporation stated that exact redox potentials for each vat dyestuff had not been determined, and, further, "There are two values which may be associated with any particular vat dye: first, the theoretical redox potential....., which is a measure of the energy required to establish an equilibrium between oxidized and reduced color; this value is of little or no interest in practical application. The second and practical value is that determined by experience; this value is always higher than the theoretical figure and represents the energy required to bring about a proper reduction of color."

It thus becomes apparent that, in connection with this study, the various published leuco potentials of individual dyestuffs are of value only as a guide to the selection of dyestuffs on the basis of low and high leuco potentials. It has been found in the experimental work that there is no close or consistent correlation of published leuco potentials with adaptability to dyeing in sulfoxylate systems. This is in contradiction to the obvious initial prediction that those dyestuffs with low leuco potentials would be most readily and satisfactory dyed with a reducing agent which is considered weaker than hydro at normal dyeing temperatures. The only correlation of this nature appears to be the fact that dyestuffs of lower leuco potentials are reduced more quickly with sulfoxylate and at lower

TABLE IV*

YARN DYEING WITH VAT DYESTUFFS

REDUCTION WITH BOTH SODIUM SULFOXYLATE FORMALDEHYDE AND HYDROSULFITE

No	Yarn		Dyes		Chemical Additions				Initial Redn				Cooling	Final Redn		
	Count	Type	% owf		NaOH % owf	Sulfox-form % owf	Temp °F	Time mins	Temp °F	Time mins	Temp °F	Time mins	Temp °F	Hydro % owf	Temp °F	Time mins
1)	24/2	KPW	20	Indanthrene Direct Black CHF	8	5	120	8	160	8	170	16	140	4	140	24
2)	37/2	CPM	6.24	Indanthrene Navy Blue BRP	8	6	130	8	170	8	190	8	140	5	140	40
			1.94	Calcoloid Direct Black JD Dbl												
			1.06	Ponsol Green 2 BLD Dbl												
3)	24/2	KPW		Calcoloid Grey 2G Dbl Ponsol Violet ARD Dbl Calcoloid Brown BR Dbl	6	5	130	8	160	8	170	8	130	4	130	32
4)	20/2	KPM		Indanthrene Yellow PGWP Dbl	5	4	140	8	160	8	170	16	140	1	140	24
5)	24/2	KPW		Calcoloid Brown BR Dbl Amanthrene Flavone GC Dbl	6	5	130	8	160	8	170	16	140	3	140	24
6)	11/1	KP	8.5	Carbanthrene Blue BCF Dbl	10	5	130	8	160	8	190	16	140	4	140	32
7)	30/2	KPM		Indanthrene Navy Blue BRP Ponsol Jade Green Supra D Dbl	8	5	140	8	160	8	190	16	140	4	140	32
8)	36/2	KPM		Ponsol Jade Green Supra D Dbl Amanthrene Flavone GC Dbl	7	5	130	8	160	8	170	16	130	4	130	32
9)	37/2	CPM		Cibanone Brill Green 3G Dbl Ponsol Green 2 BLD Dbl Indanthrene Yellow PGWP Dbl	8	6	130	8	160	8	170	16	140	5	140	40
10)	36/2	KPM		Carbanthrene Blue BCF Dbl	10	5	130	8	160	8	170	16	140	4	140	32

* Dyeings are shown in Figure 2. Sequestering agent and 4% WC Dextrine owf was added for all dyeings. Dyeings were oxidized and soaped. Test dyeings were knit from inside, outside, and middle of pkg from top to bottom of swatch. Goods were prescoured with outside-in circulation at initial indicated temperature. Circulation of pigment was outside-in for 16 minutes. Production dyeings were made with 550-lb loads in Gaston County Package Machine at bath ratio of about 8:1 with cycles of 6 minutes' outside-in and 2 minutes' inside-out circulation.

pH values. It should be emphasized that, in our work, the studies of Lineken et al *(9)* in connection with leuco potentials proved invaluable and is considered essential towards an understanding of the significance of reduction potentials in dyeing. The observation that reduction with sulfoxylate is to a greater degree a function of time than of temperature or alkalinity (which are also important factors) is graphically illustrated by testing a dyebath of known reduction potential of 1,000-1,200 millivolts with Vat Yellow G test paper, which has a leuco potential of less than 800 millivolts. The paper does not begin to turn blue unless it remains in the bath for a period of at least ten seconds, whereas, in a hydro solution of lower potential, the color change is immediate.

Figure 1 represents typical dyeing curves for both hydro dyeings and sulfoxylate dyeings under otherwise constant conditions, in which redox potential is plotted aaginst time. This is merely a reproduction of composite data recorded. It is seen that, with hydro, immediate high potentials are developed at low temperatures, and with increased temperature the increase in potential is developed at a moderate rate, while decreased temperature reduces the potential at a very slow rate. However, with sulfoxylate, the initial potentials developed at low temperatures are much less than with hydro, but a rapid increase in potential occurs as temperature increases, and a moderately rapid decrease in potential occurs as temperature decreases.

The most significant features of this comparison, which may be considered pertinent to dyeing applications, appear to be as follows:

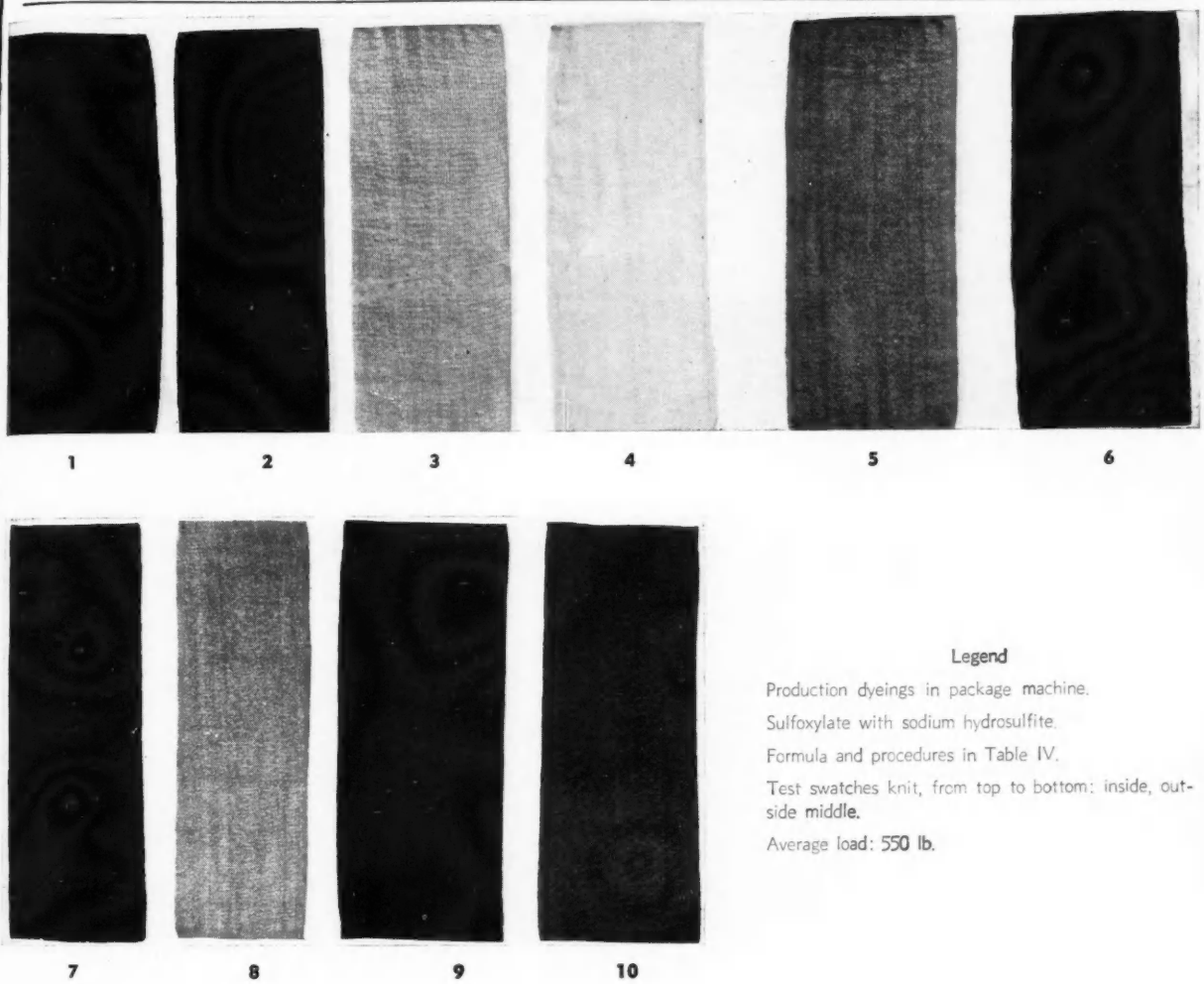
1) The maintenance of potentials with sulfoxylate, comparable with hydro potentials, at desirable temperatures.

2) The gradual reduction to the leuco, which appears to be a function of time-temperature and thus can be controlled by temperature in producing moderate or complete reduction in a desired period of time.

3) The initial high-temperature stability of the sulfoxylate, which makes possible the maintenance of high reduction potentials at high temperatures for protracted periods of time without fear of a sudden drop in potential and oxidation of the leuco.

INITIAL LABORATORY DYEINGS ———Preliminiary dyeings on cotton indicated that, for light to medium-light shades, practically all vat dyes tested were satisfactory for application with sulfoxylate as the reducing agent. It was noted that the dyeings were equal in quality to or better than the hydro control dyeings, and many of the sulfoxylate dyeings were strikingly superior in quality. In medium to heavy shades, though many of the sulfoxylate dyeings were considerably weaker in color value, with the majority of the dyestuffs which fell into this class, comparable color value was obtained by using a small quantity of hydro for a short period of time at the end of the dyeing cycle. In such cases the total quantity of reducing agent did not exceed the total quantity of hydro normally used in conventional hydro application.

In order to simplify the study, the use of leveling agents or retarders was avoided, so that the standard dyebath



Legend

Production dyeings in package machine.

Sulfoxylate with sodium hydrosulfite.

Formula and procedures in Table IV.

Test swatches knit, from top to bottom: inside, outside middle.

Average load: 550 lb.

Figure 2
Yarn dyeing

consisted of sodium hydroxide, a wetting agent, a sequestering agent, and the reducing agent or agents. Sodium carbonate was used in some dyeings as a buffering agent. The leuco stabilizing agents "WC" dextrine and sodium nitrite were used, and, in package dyeing a dispersing agent sometimes, particularly when it was deemed necessary because of the fact that the dyestuff was not classified as a dispersed type suitable for the pigment method. Salt was also used on some dyeings where substantivity was not high.

The following further observations were made on the sulfoxylate dyeings compared with hydro controls:

a) Some dyestuffs, which gave unsatisfactory results with hydro under certain conditions, could be dyed simply and satisfactorily with sulfoxylate under the same conditions. This was particularly true of light shades with the most highly substantive dyes of the "IN" group, such as Anthraquinone Vat Jade Green and other rapidly exhausting dyes, such as Anth Vat Gray R (Anthraquinone).

b) Increased color value was obtained with several dyestuffs, for example, Indigoid Vat Scarlets 2B and 2G, Anth Vat Navy Blue, Hydron Blue, the halogenated indanthrones, and Anth Vat Dark Blue BO.

c) Distinctly different oxidized vat shades were noted with several dyes, for example, Indigoid Vat Orange R, Indigoid Vat Red 3B, Anth Vat Yellow R, Anth Vat Dark Blue BO, the indanthrones, Anth Vat Olive Green B, Anth Vat Gray R, Anth Vat Black BBD, and Anth Vat Brilliant Violet 4RN.

d) A significant loss in color value was noted for many dyestuffs, particularly in heavy shades, for example, Anth Vat Yellow GC, Anth Vat Yellow R, Anth Vat Orange RRT, Anth Vat Red BN, Indigoid Vat Red 3B, Anth Vat Olive R, Anth Vat Brown G, and Anth Vat Khaki 2G.

e) Distinctly different leuco colors were noted with several dyestuffs, either at an intermediate stage or at the final reduction stage, for example, Anth Vat Blue BF, Anth Vat Yellow GC, Anth Vat Dark Blue BO, and Anth Vat Black BB.

SULFOXYLATE—HYDRO PRODUCTION DYEINGS ON YARN———In Figure 2 (data in Table IV) *(9)* are seen production dyeings made on the package machine with sulfoxylate as the primary reducing agent and with added hydro. The dyeings were characterized by excellent levelness, penetration, and minimized crossovers, particularly on the inside of the package next to the tube, where penetration is normally poor with some dyes. The dyeings were considered better in quality than similar shades previously

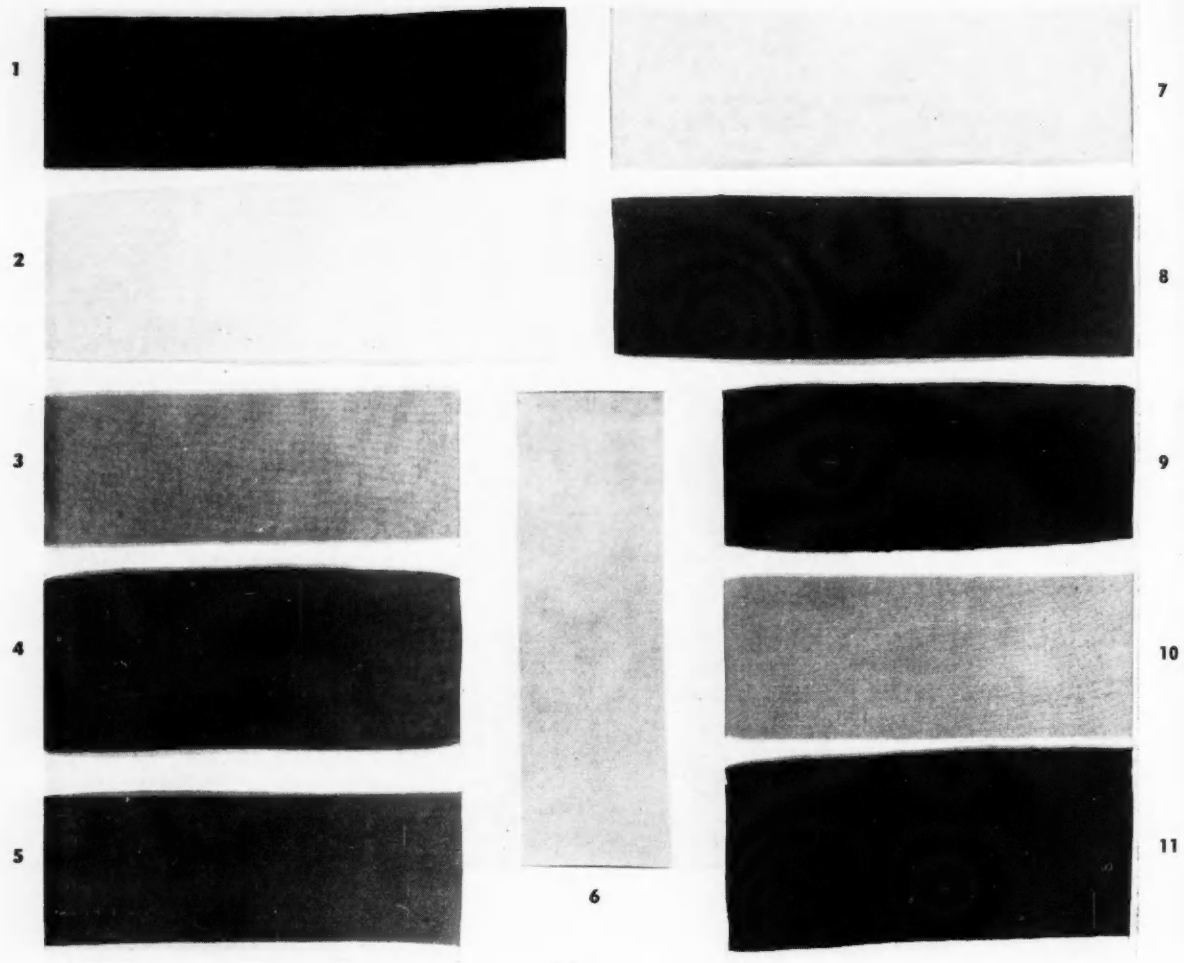


Figure 3
Yarn dyeing with sulfoxylate—no hydro

dyed with hydro alone. A striking improvement in quality was noted with dyeings of Anth Vat Blue BF (C I 1113).

It appears from results of later work that the additional color value imparted by the addition of hydro at the last stage of the dyeing cycle might be due primarily to the lowering of the pH value resulting from the evolution of acidic decomposition products, since the reduction potential is increased only very slightly by the hydro.

SULFOXYLATE PRODUCTION DYEINGS ON YARN———In the yarn dyeings made with sulfoxylate (Figure 3 and Table V) the quality was excellent and there appeared to be no serious economical or processing disadvantages. An advantage, in addition to slowed exhaustion rate in producing good levelness, was thought to be increased stability of the reducing agent, eliminating the need of testing for reduction at any stage after the dyestuff is initially reduced. It is to be noted that, in dyeing by the pigment method, which appears to be slightly preferable over the reduced method, it is perhaps more critical than with hydro dyeings to pigment with a good dispersion, since agglomerated dyestuff particles are more difficult to reduce with sulfoxylate.

The specific conditions of application, including the inclusion or elimination of a scouring operation, are determined largely by the behavior of the pigment particles of the dyestuffs used during the pigmenting phase of the procedure. The set of conditions for a single dyestuff or for a specific combination used in a formula which results in the attainment of a well-dispersed dyebath at the moment of initial reduction is the ideal for that specific formula.

With most dyestuffs, this ideal condition is attained through the following sequence:

1) Scour the package with a low titer soap and an alkali.

2) Refill machine, heat to 130 F, add dissolved low titer soap. Disperse the dyestuff with soap as a dispersant, and add to machine. Circulate 10-20 minutes outside-in and add dissolved caustic.

3) Add 4-8% sulfoxylate.

4) Heat slowly to 160-80 F, until reduction begins.

As the dyestuff of lowest reduction temperature is fully reduced, the other dyestuffs should remain well dispersed and are subsequently slowly reduced by raising the temperature. After complete reduction the dyeing is completed by running at temperatures varying from 160 to 200°F for periods of 20 to 45 minutes, depending upon the exhaustion rates of the dyestuffs.

TABLE V*

YARN DYEING WITH VAT DYESTUFFS
REDUCTION AND DYEING WITH SODIUM SULFOXYLATE FORMALDEHYDE

No	Yarn		Dyes		Chemical Additions outside-in at 130°F			Reduction Stages				Dyeing Stage		Redox Pot
	Count	Type	% owf		NaOH % owf	Na_2CO_3 % owf	Sulfox-form % owf	Temp °F	Time mins	Temp °F	Time mins	Temp °F	Time mins	Mv
1)	11/1	KP	13.0	Hydron Blue	3	4	8	170	8	180	16	180	40	1125
2)	36/2	CPM	0.04	Indigoid Vat Pink FF	7	1	6	130	10	160	20	200	32	1080
3)	8/1	KP	1.0	Indigoid Vat Brown G	3	1	5	130	10	160	10	200	24	1050
4)	14/1	KP	1.0	Anthraquinone Vat Grey R	8	1	7	150	8	170	15	190	32	1180
5)	36/2	KPM	0.5	Anthraquinone Vat Blue BF Dbl	10	0	8	160	8	170	16	190	32	1240
6)	36/2	KPM	0.15	Anthraquinone Vat Blue BF Dbl	10	0	6	160	8	170	16	190	32	1130
7)	24/2	KPM	3.0	Anthraquinone Vat Yellow PGA Dbl	7	0	7	160	8	170	8	190	32	1110
8)	36/2	KPM	20	Anthraquinone Vat Jade Green Dbl	7	0	7	160	8	170	8	200	32	1160
9)	11/1	KP	8.7	Indigoid Vat Brill Blue 4B	3	4	8	140	8	160	8	200	40	1190
10)	30/2	KPM	0.25	Anthraquinone Vat Jade Green Dbl	7	0	7	160	8	170	8	200	32	1185
			0.45	Anthraquinone Vat Yellow GC Dbl										
11)	18/1	KP	5.0	Anthraquinone Vat Blue BF Dbl	12	1	9	160	8	170	16	190	32	1210

* Dyeings are shown in Figure 3. A sequestering agent and 4% WC Dextrine owf were added for all dyeings. Goods were prescoured with outside-in circulation at initial temperature indicated. Circulation of pigment was at 130°F with outside-in flow for 16 minutes. Dyeings were made with 550-lb loads in Gaston County Package Machine at bath ratio of about 8:1 with cycles of 6 minutes' outside-in and 2 minutes' inside-out circulation. Test swatches were knit as in Table IV.

Certain dyestuffs, after initial reduction is carried out at elevated temperatures (180-200°F), were found to possess maximum affinity at lowered temperatures, at which good reduction is maintained. Thus, the final dyeing stage is accomplished at reduced temperatures, equipment permitting. Examples are Anth Vat Blue BF (C I 1113) and Hydron Blue (C I 969) with maximum affinity at 155-165°F; and Indigoid Vat Brill Blue 4B (C I 1184) with maximum affinity at 105-115°F.

5) The dyebath is then dropped, the goods are given a running wash, oxidized, soaped off, and finished as usual.

Variations in this sequence are advisable where the characteristics of the dye dispersion indicate that a change in sequence results in a more stable dispersion prior to reduction or, if desired, a more gradual reduction.

For very light shades and for heavier shades with some dyes it is preferable to add the pigment first at a moderate temperature, then to add the sulfoxylate, which effects a gradual reduction as the temperature is slowly raised. In other cases the dye pigment remains dispersed better if the alkali is added 10 to 20 minutes after initial dispersion at the reduction temperature or higher. Sometimes dispersion stability is optimum if part of the sulfoxylate is dissolved and added with the caustic soda at the reduction temperature.

In all cases in setting up a formula and procedure, it is recommended to start with the quantity of caustic soda normally used with hydro and with sulfoxylate replacing hydro pound for pound. This quantity in some cases is reduced by 20 to 30%, particularly if the period of reduction or dyeing is long.

The above five-step procedure for cotton is varied for viscose rayon by substituting the following procedure for Step 4:

4) (for rayon). After the dyestuff is completely reduced, acetic acid or monobasic sodium phosphate is slowly added to reduce the pH range to an optimum of 7.5-8.5 for indigoids and 9.0-10.0 for anthraquinone types, at which values the dyeing is carried out to completion. Or, if it is desired to further reduce swelling, a reduced method can be used wherein the reduced dyestuff solution is adjusted to the lowered pH ranges and added to a spring bath of approximately the same pH value, at temperatures of 160-180 F.

HYDROSULFITE CONTROL DYEINGS*———In Figure 4 and Table VI laboratory sulfoxylate dyeings were compared with hydro control dyeings. The hydro dyeings were made under conditions specified as optimum by the various dyestuff manufacturers, some being dyed in the manufacturer's laboratory and some in our laboratory. Where two hydro dyeings are shown, there was a stubstantial difference in the dyeings made by two or more different manufacturers, supposedly of prototype dyes in equivalent strengths. Most of the hydro control dyeings were made at temperatures of 130-140°F. The application conditions for the sulfoxylate dyeings are not to be considered optimum but are listed as a guide to adaptability.

EVALUATION OF VAT DYESTUFFS FOR SULFOXYLATE APPLICATION———In Table III evaluations are made of sulfoxylate dyeings with those dyestuffs on which a sufficient number of reasonably consistent results were obtained under variable conditions. The tabulations do not represent a single dyeing condition but are an effort at representing composite results of approximately 900 laboratory dyeings at various concentrations for the 49 dyestuffs listed on both mercerized and unmercerized cotton.

Though reduction potential is affected by alkalinity, alkalinity was not found to be a critical factor in attaining sufficiently high reduction potentials and seemed rather to be important in influencing affinity and depth of shade. Temperature and time are also important in gaining exhaustion and depth of shade. The temperatures of optimum affinity for individual dyestuffs often vary from those established for hydro. Since sulfoxylate reduction does not occur at low temperatures, dyeing often may be carried out at a lowered temperature. Since an inherent characteristic of most of the leucos

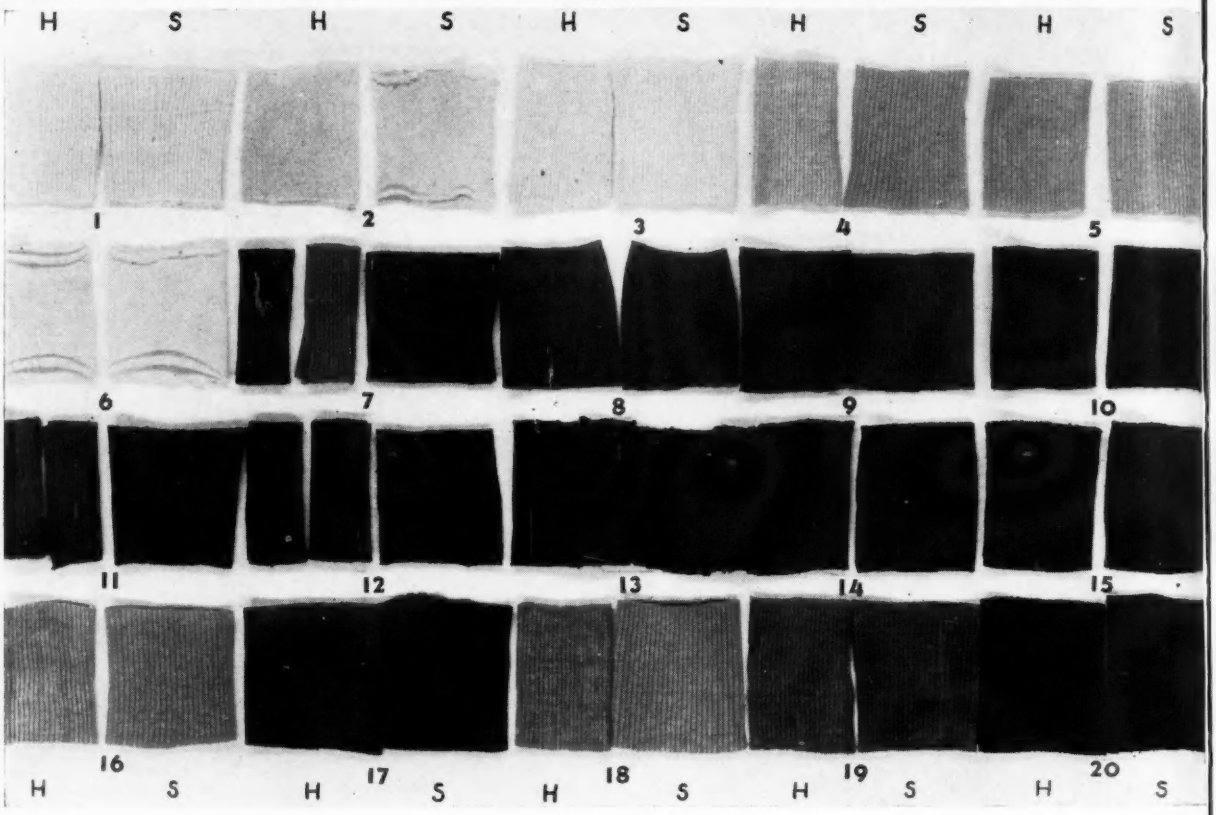


Figure 4

Comparison of sulfoxylate dyeings with hydro dyeings (on cotton)

formed with sulfoxylate is slow exhaustion, more dyeing time is usually required than for hydro leucos. This is no problem for light shades, but for heavy shades, dyeing time must be lengthened to obtain full depth. It is further to be noted that temperatures in the range of 210-250°F did not appear to promote exhaustion as much as was indicated by the behavior at lower temperatures, but the stability of the leucos at those high temperatures was good.

Dyeing was limited to a period which was considered practical and economic. In the case of those dyestuffs that did not approach full color value within practical time limits, full depth was obtained in most cases by the addition of small quantities of hydrosulfite for a very short time at the end of the dyeing cycle. Under such conditions, when the desired depth was obtained, even if the hydro was consumed before the end of the cycle, the depth was retained and the dyestuff was kept in reduction by the action of the sulfoxylate. In dyeing compound shades in which two or more dyestuffs of widely varying substantivities were used, the variations in the exhaustion rates appeared to be minimized with sulfoxylate. This was verified by making "strike" tests at various dyeing stages, and the shades obtained at the end of the cycle appeared considerably closer to the initial shade than for hydro dyeings of the same dyestuffs. In summarizing, it thus appears that rate of exhaustion can be controlled by control of alkalinity, temperature, and time. Although in general good reproduceability was obtained, the experiments wer not void of anomalies, for example, in the dyeing of extremely light shades of some colors where dye concentrations were very low, reduction did not occur as readily or rapidly, at constant reduction potential, temperature, and alkalinity, as in a more concentrated dispersion of the same dye. As difficulties of this nature were thought to be attributable to interfering metallic ions, they were minimized by increasing the quantity of sequestering agents.

In the dyeing of mercerized cotton, optimum affinity of many of the leucos for the fiber did not occur at the same high alkalinities as for unmercerized cotton. This did not seem to occur with dyestuffs for which optimum affinity was at low or medium alkalinities, and thus no general relationship between optimum alkalinities for unmercerized fiber as compared with mercerized fiber could be predicted with as much confidence as for dyestuff affinity in general. This phenomenon might be caused by some physical or chemical property peculiar to mercerized fiber and must be considered too complex to be within the scope of this study. The general study pertaining to optimum application conditions was thus primarily confined to unmercerized cotton, though specific practical formulae for dyeings on mercerized goods and data for other fibers are given in preceding section. In general, however, the quantity of alkali necessary for the best reduction and dyeing on mercerized cotton was in the range of 50 to 75% of the amount required for a dyeing of the same strength of unmercerized fiber.

Some dyestuffs of poor adaptability but which manifested good experimental reproduceability were included in this table in order to aid those who desire to utilize the data for practical work and who might select dyestuffs other than those that appear to be best adapted to the method.

Dyeings were made on knitted tubing at a 20:1 bath ratio and on yarn on 1⅝" tubes in the package dyeing machine at bath ratios of 10:1 and 8:1. There were no contraindications to adaptability of the data in any case to applications at bath ratios of 8:1 and 10:1. Initial dyeings

TABLE VI*

LABORATORY METHODS FOR THE SULFOXYLATEFORMALDEHYDE DYEINGS OF FIGURE 4

No	Dyes		Notes	Bath	Reduction					(Dyeing Stages)				
	% owf			Ratio	NaOH % owf	Na_2CO_3 % owf	Sulfox-form % owf	Temp °F	Time mins	Temp °F	Time mins	Salt % owf	Temp °F	Time mins
1)	5.0	Anthraquinone Vat Yellow GC Dbl		20	20	5	10	170	10				200	30
2)	3.0	Anthraquinone Vat Yellow PGA Dbl	(m)	8	20	0	15	150	10				190	30
3)	5.0	Indigoid Vat Orange R		20	5	2	10	150	10				200	30
4)	3.0	Indigoid Vat Scarlet 2G		20	15	5	15	160	10			15	200	25
5)	5.0	Indigoid Vat Scarlet 2B		20	15	5	15	160	10			15	200	25
6)	0.04	Indigoid Vat Pink FF Dbl	(e, m)	8	7	1	6	130	10	160	20		200	32
7)	1.5	Anthraquinone Vat Brill Violet 4RN Dbl		20	30	0	20	170	10				200	20
8)	2.0	Anthraquinone Vat Jade Green Dbl	(c, m)	20	20	0	15	160	10	200	5(a)		170	20
9)	2.5	Anthraquinone Vat Jade Green Dbl		20	30	5	15	160	10				200	20
10)	8.0	Indigoid Vat Brill Blue 4B		20	5	2	18	180	20					
11)	3.0	Anthraquinone Vat Blue BF Dbl		20	25	5	20	160	20					
12)	5.0	Hydron Blue		20	5	2	15	160	10			20	200	20
13)	13.0	Hydron Blue	(b, d)	8	3	4	12	170	8	180	16	10	180	40
14)	5.0	Anthraquinone Vat Navy Blue Dbl		20	20	0	15	160	10				200	20
15)	2.0	Anthraquinone Vat Dark Blue BO Dbl		20	20	0	18	160	10				200	20
16)	1.0	Anthraquinone Vat Brown BR Dbl		20	25	5	15	160	10				200	20
17)	5.0	Anthraquinone Vat Khaki 2G Dbl		20	40	20	20	160	10				200	20
18)	1.0	Anthraquinone Vat Gray R		20	25	5	12	160	15				200	15
19)	1.0	Anthraquinone Vat Gray GNF		20	25	5	12	160	15				200	15
20)	15.0	Anthraquinone Vat Black BBD		20	20	0	20	160	10				200	25

NOTES:
(a) 25% of 28% acetic acid owf added at this point.
(b) The hydrosulfite control was run on mercerized goods with 15% dye.
(c) Better yield on mercerized goods.
(d) Better yield in a short bath.
(e) The hydrosulfite control was run with 0.07% dye.
(m) Mercerized cotton.
(owf) On weight of fiber.
* Dyeings are shown in Figure 4.

were made on prescoured, prebleached, and on unscoured goods. Where a wetting agent was used for unscoured goods, there appeared to be no substantial difference in the quality or color value of the dyeings. In order to approach a practical ideal water condition that could be met by any dyehouse, a sequestering agent was selected and used which would chelate all of the commonly encountered metallic ions known to cause interference in dyeing. A wetting agent was also selected for stability and efficacy within the alkalinity range of the experiments. Consequently, final check dyeings were made at 20:1 on unscoured goods. Package goods were prescoured 30 minutes at 190°F before dyeing. Observations made during the progress of the dyeings showed that, once the near-optimum quantities of dyeing reagents and the initial reduction potential had been determined, the dyeing reduction potential and the rate of exhaustion could be varied at will by temperature control. Though the initial reduction potentials were probably well above the range of the particular dyestuff as established in a hydro system, and also high enough to be considered above the apparent leuco potential for the sulfoxylate system, immediate reduction did not take place as in the hydro systems. Not only was the dyeing itself a function of time-temperature, but the change to the leuco form was also to a very great degree a function of time as well as of temperature. This phenomenon was indicated by the fact that, in a system in which a high reduction potential had been developed at a constant temperature, no immediate reduction was seen, but a gradual reduction took place as observed by the change to the leuco color. This change had been observed in some systems first in the pigmented goods, then on the dispersed particles; in other systems, the dispersed particles, not dispersed on the fiber, appeared to be reduced before the deposited particles. It is possible that this was due to variation in particle size or dispersibility.

The excellent penetration and levelness attained was apparently due to the low initial rate of exhaustion. In a batch-type operation two factors are to be considered in explaining the levelness and penetration, notwithstanding the rapid exhausting and poor leveling properties of some of the dyestuffs. The first is the slow rate of reduction of the dyestuffs at the initial leuco potential; the second is the apparent slower initial rate of exhaustion, which appears to be characteristic of the sulfoxylate systems. The "strike" or initial dyeing rate appears to be significantly less than in a hydro system. Samples immersed in the dyestuffs at or near the initial leuco potential gave a decidedly decreased "strike" than those immersed at higher potentials; however, even when immersed at high temperatures (200-210°F) and high potentials (1200 mv or over) for short periods of time (1 to 60 seconds), the dyeings were well penetrated, and the general quality, including level-

ing, was good. Further evaluative work, which was not completed in time to be included in this paper, will include specific data on dyestuffs applied by the sulfoxylate method evaluated quantitatively according to the method presented by Skinkle et al *(10)*.

In the early stages of this study the importance of the pH factor with reference to optimum absorption of the leuco by cellulosic fibers was not given the consideration which later progress indicated to be necessary. During the initial work high and low alkalinities were used as starting points in determining optimum alkalinities without regard to very low alkalinities in which, by the use of buffering agents, pH values in the range of 8 to 12 are reached. Later work, which includes attempts at determination of optimum pH values for individual dyestuffs in attaining maximum absorption on cellulosic fibers, was not complete enough to be included in this paper. The general technique, however, is the following method *(9)*, dyestuff is reduced in a sufficiently alkaline bath to obtain complete and stable reduction, dyeing is begun at a high pH, then, by addition of weak acids and/or buffering agents, the pH is gradually reduced to the range established as optimum for the dyestuff and fiber, and dyeing is continued until the desired exhaustion is attained.

STABILITY OF INDANTHRONES AT HIGH TEMPERATURES——Although a considerable amount of valuable work has been done in the general field of the stability of vat dyestuffs at elevated temperatures *(11)* *(12)*, particularly on the indanthrones, the effect of sulfoxylate versus hydro was apparently not previously studied thoroughly. In the prize-winning study of the Piedmont Section in 1948 *(11)*, sulfoxylate reduction was mentioned, but was not studied in this connection because of its apparent unsuitability as a reducing agent in dyeing concentrations. In view of the superior dyeings obtained in the initial studies with sulfoxylate, it was deemed appropriate to make a comparison of the stability at 200°F of four indanthrones with sulfoxylate versus hydro. Dyeings are seen in Figure 5. Both the sulfoxylate dyeings, columns "S," and the hydro control dyeings, columns "H," were carried out at 200 $\pm$ 5°F for a period of 20 minutes under conditions as near optimum as possible for the temperature involved. One series was run on unmercerized cotton goods and another on mercerized goods, since it had previously been determined that the effect was dependent upon type of fiber as well as upon the other variables. In each series for four indanthrones, the dyestuff percentage was constant for each dyestuff for unmercerized goods; for mercerized goods one-half the percentage was used. All other conditions for the 48 dyeings were kept constant with the exception of the inclusion of leuco stabilizing agents for comparison. In the columns H_d and S_d, WC dextrine was used in the bath in a concentration of 0.4% (ows) or 8% (owf); in the columns H_n and S_n sodium nitrite was used in a concentration of 0.25% (ows) or 5% (owf).

It is seen in Figure 5 that the effect of sulfoxylate in promoting increased stability of leuco was good, particularly for the halogenated members of the group, C I 1112, C I 1113, and C I 1114. The effect is most exaggerated, as would be expected, when stabilizing agents are excluded (columns H and S). It is also to be noted that the stabilizing effect of sulfoxylate when used to replace hydro as the reducing agent is markedly variable with each dyestuff, with the two stabilizing agents, and with the two fibers. In all cases, however, it is seen that with sulfoxylate there is no evidence in the oxidized shade of gross overreduction resulting in the irreversible formation of the tetrahydro derivative *(1, 13)*. This is further confirmed by the observation that the tetrahydro derivative was formed and appeared in noticeable quantities in many of the hydro control dyeings, including those with each stabilizer, as a yellowish-brown substance with no affinity for cellulosic fiber, while in the sulfoxylate dyeings there was no visual indication of its formation.

The use of sulfoxylate to replace hydro as the reducing agent in high-temperature application is therefore set forth as an improved method *(9)* for dyeing of the indanthrones, both with and without leuco stabilizers. It is recognized that the stability of the indanthrones is considerably better, particularly with stabilizers, in continuous applications where the dyeing time at elevated temperatures is very short. However, even during reduction periods of short duration, such as would be used in the pad-steam process or in Williams units, thtere appears to be an improvement in stability with sulfoxylate. The improvement should be increased in applications such as the Williams hot-oil process, wherein higher temperatures are used. Although there were strong indications that the use of sulfoxylate improved the high-temperature stability of the vat dyes of other classes, the differences as compared with hydro controls were not as great as with the indanthrones. This was particularly true with the dyeings run at a 20:1 bath ratio in which experimental difficulty was encountered in obtaining overreduced dyeings with hydro; in more concentrated dye baths overeduction was more pronounced.

CONTINUOUS DYEING——The bath ratios used in the experiments were wide enough in range to indicate good adaptability to any batch-type operation or equipment, including jig and beck. In lower bath ratios and high concentrations, such as are commonly used for the continuous dyeing of woven piece goods, the method was evaluated only to the extent of determining that the apparent advantages were similar in concentrated dyebaths, for example, low strike and increased high-temperature stability. If one of the methods is used whereby the goods is padded through a high-temperature reduced bath, it was determined that sulfoxylate alone could be utilized as the reducing agent in light to medium shades but that in heavy shades initial reduction with some dyestuffs should be made with hydro, and sulfoxylate should be used for the maintenance of reduction potential thereafter.

Adaptability to batch-type operations in the reduction state would obviously apply to any of the noncontinuous-type applications, such as the pigment-pad jig-reduced method. In continuous methods the same advantages would apply and the additional minimization of difference in exhaustion rates would be of more value. Except for reduction at very high temperatures, ie, over 212°F, the sulfoxylate method would probably present the disadvantage of requiring more time in reduction, which would necessitate changing the existing equipment if no sacrifice in speed was permissible. This has not been experimentally proven but is indicated by a moderate amount of laboratory data, which were considered insufficient to be tabulated in this study. The method of using sulfoxylate both with and without hydro *(9)* on various pigment pad equipment in conjunction with booster boxes and Williams Units and in the pad-steam, hot-oil and Standfast processes or combinations thereof, is considered as possessing similar advantages for continuous dyeing as for applications previously mentioned. In the continuous dyeing of viscose rayon the additional advantage of better control of the pH factor is considered significant.

VISCOSE-RAYON APPLICATION——Because of the great affinity of most vat dyes for viscose rayon and the swelling action of alkalis *(1)*, the sulfoxylate method without hydro *(9)* appears to be most promising for difficult applications, such as the dyeing of yarn packages, cakes, beams, and raw stock, by virtue of its ability to control exhaustion and to maintain the desired reduction potential and because of the ease with which the pH can be controlled. The problem of attaining color value encoun-

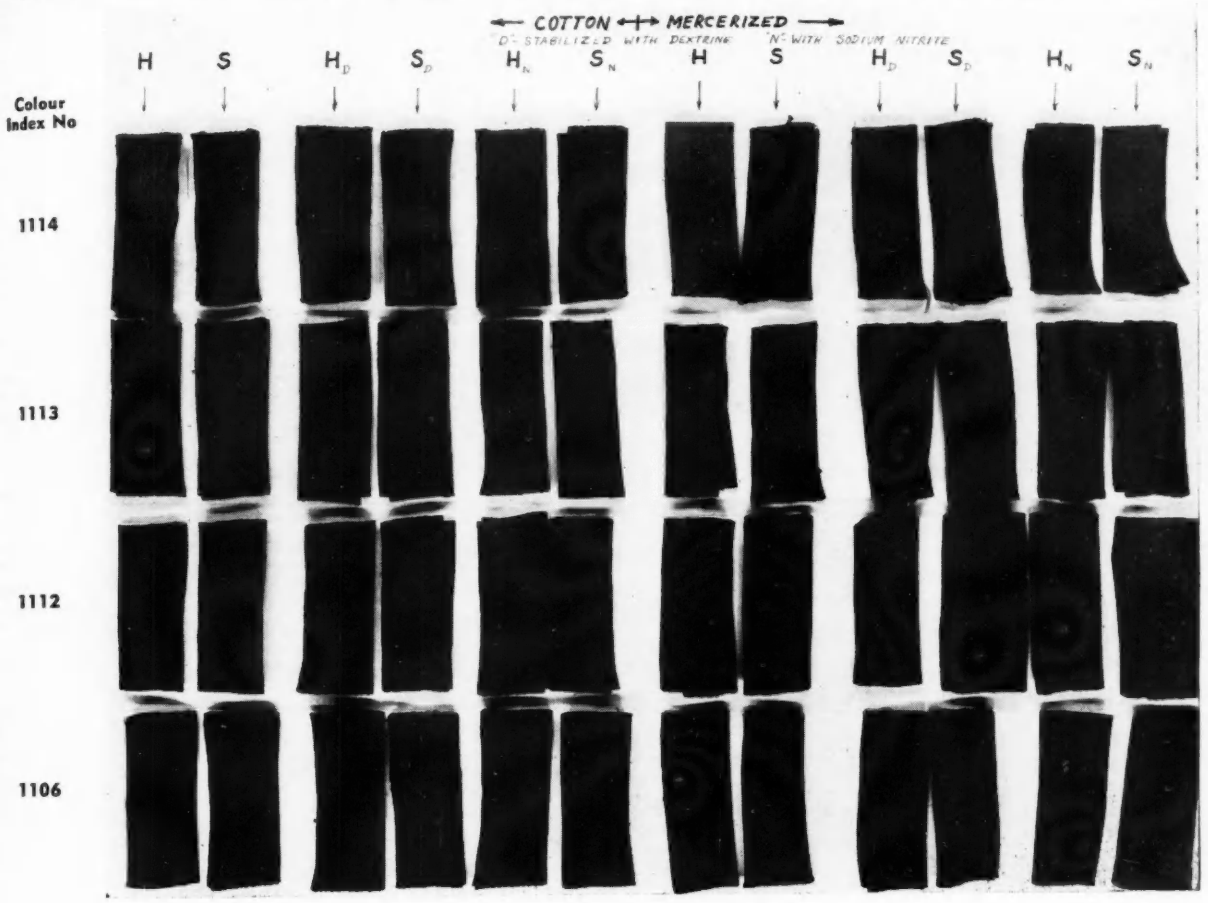


Figure 5
Stability at 200°F of Indanthrones —— Reduction with sulfoxylate vs hydrosulfite

tered in the dyeing of cotton with certain dyestuffs was not found to be so difficult in the dyeing of viscose. However, the most easily workable pH ranges were found to be critical and varied with individual dyestuffs. The pH range of maximum affinity in general for indigoid types was 7.5 to 8.5 and for anthraquinones 9.0 to 10.0. For batch-type application, as illustrated by dyeings in Figure 6 on staple fiber, near optimum conditions appeared to be as follows:

1) Pigmentation at 130-140°F.

2) Addition of small quantities of caustic soda buffered with sodium carbonate in sufficient quantity to effect reduction, depending upon the dyestuff, together with the sulfoxylate.

3) Moderately gradual rise in temperature to 160-190°F (varying with dyestuff).

4) At the point of complete reduction, acetic acid or monobasic sodium phosphate is added very slowly to reduce the pH to the optimum ranges noted above.

Thus a gradual exhaustion takes place in two stages—during the initial reduction, as temperature is raised, and during the dyeing at 160-180°F, as the pH is lowered. The dyeings in Figure 6 were made by this method on staple fiber. A similar method *(14)*, in which a variation of the Abbott-Cox method *(1)* is used, accomplishes a partial reduction of the pigmented dyestuff on the fiber by addition of soda ash and hydrosulfite.

IMPORTANCE OF PIGMENT DISPERSIBILITY———In all applications of sulfoxylate reduction, a most important factor is the selection of easily dispersible vat pastes or powders, especially in batch-type applications where the pigment method is preferable. A good dispersion of the vat pigment prior to reduction is essential to the attainment of a controlled and uniform rate of reduction.

It was found that there was a great variation in the dispersibility of various vat dyestuffs and of individual dyestuffs of different manufacture. Whether these differences were caused by particle size or other inherent physical or chemical properties of the pigments or whether they were caused by interference from external additive materials, such as dispersers, was not determined.

As a test for dispersibility, cotton yarn wound in 1⅝" perforated steel tubes was pigmented in a laboratory package dyeing machine, and observation were made on the dye dispersion and on the package prior to reduction to determine if and when agglomeration occurred. Those conditions which resulted in good dispersions without agglomeration or deposition on the package prior and during complete reduction were considered good.

Indicating the wide variations in dispersibility behavior of the various dyestuffs, about ten different methods of application appeared to be good for one or more dyestuffs, but none resulted in freedom from premature agglomeration with the majority of the dyestuffs used.

One of the best dispersing agents was found to be a low titer soap, which appeared to disperse well under wide variations in application technique.

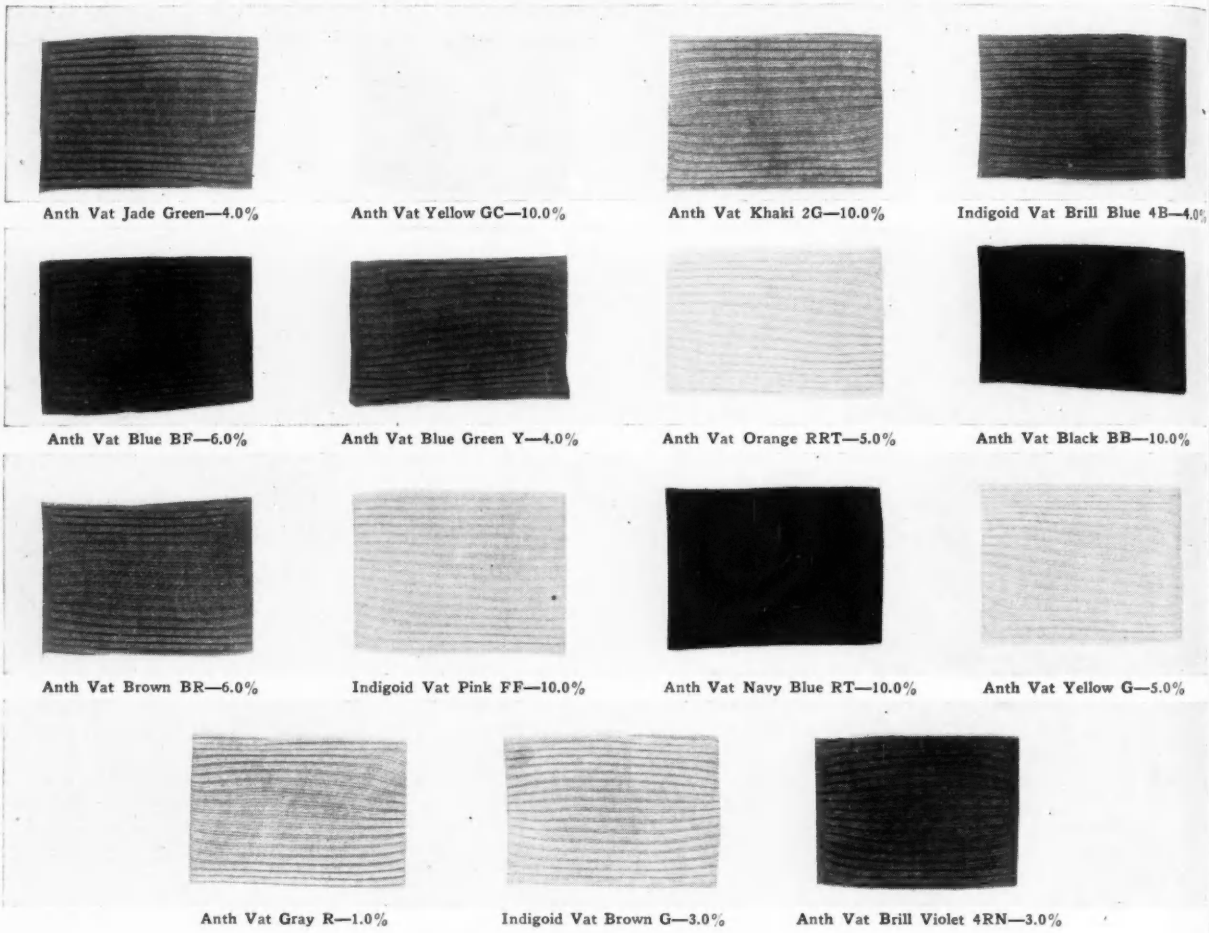

Anth Vat Jade Green—4.0%
Anth Vat Yellow GC—10.0%
Anth Vat Khaki 2G—10.0%
Indigoid Vat Brill Blue 4B—4.0%
Anth Vat Blue BF—6.0%
Anth Vat Blue Green Y—4.0%
Anth Vat Orange RRT—5.0%
Anth Vat Black BB—10.0%
Anth Vat Brown BR—6.0%
Indigoid Vat Pink FF—10.0%
Anth Vat Navy Blue RT—10.0%
Anth Vat Yellow G—5.0%
Anth Vat Gray R—1.0%
Indigoid Vat Brown G—3.0%
Anth Vat Brill Violet 4RN—3.0%

Figure 6
Viscose rayon staple dyed with sulfoxylate at 20/1

SPECIAL APPLICATIONS

VAT-ACID REDUCTION ——— The greater stability of sulfoxylate as compared with hydro at all temperatures and over a wide range of alkalinity and acidity was found to be advantageous in the production of acid vats or hydrolyzed leucos and applications thereof *(9)*. Moreover, the hydrolyzed leucos formed with sulfoxylate appeared to be more desirable in physical and/or chemical properties than those in which hydro was used as the reducing agent. Both the absorption and stability of the sulfoxylate acid leucos was better, this phenomenon perhaps being due to difference in particle size or solubility and to an equilibrium relationship between intermediate hydrolyzed stages. Another possible explanation could be that there was a hydrotropic effect *(20)* on the acid leuco by the sulfoxylate solution. Observations of variations in affinity indicated that the sulfoxylate vat acid is different from the hydrosulfite vat acid. Conversion from the basic leuco to the acid leuco seemed to be stabilized and aided by the presence of the goods in some cases where it appeared difficult to obtain a complete vat acid from a solution of the sulfoxylate basic leuco. In such cases there appeared to be an incomplete formation of the basic leuco, possibly because of a salting-out effect of the unreduced dispersion at the neutral point, at which normally the acid leuco is produced. It was found that added color value was obtained by a partial initial dyeing of the fiber with the basic leuco, then converting to the acid leuco until exhaustion was reached—as opposed to the more direct process of dyeing in all stages with the acid leuco or with the basic leuco throughout the process. It was established that, for many dyeing conditions, the minimum pH must be in the range of 7 to 8, and that loss of color value is noted if the final pH is permitted to drop further. With some dyestuffs it appeared possible to obtain a stable acid leuco in one step directly from the oxidized form of the vat, rather than to obtain the normal sodium enolate or alkaline leuco form first and then, by acidification, to convert to the hydrolyzed leuco. In all cases the acid leuco obtained with sulfoxylate, either by the direct method or by acidifying the normal alkaline leuco, resulted in acid leuco states which evidenced increased stability over a wider pH range and a wider temperature range than those in which hydrosulfite was used. This advantage can be utilized in any of the conventional vat-acid applications *(1, 13, 20)*. The application of acid leucos *(15)* and partially hydrolyzed, or "intermediate" leucos, without subsequent alkaline reduction was explored, and the applications *(9)* are briefly discussed in the foregoing section. It is to be noted that, with sulfoxylate, stable acid leucos can be formed and maintained at a pH of 7.0 or slightly above this value.

CELLULOSE ACETATE AND NON-CELLULOSICS——During the latter stages of this investigation it was determined that, not only for cellulosics, but for the noncellulosics tested, the pH factor was of great importance in approaching optimum absorption of dyes, especially in the instances of individual dyestuffs which exhibit poor affinity and the various fibers which possess poor absorption characteristics. Satisfactory dyeings of good depth were obtained with variations *(9)* of the alkaline sulfoxylate, vat-acid sulfoxylate and "intermediate hydrolyzed" sulfoxylate methods under the conditions that follow, which apply in general to both indigoid and anthraquinone-type vat dyes.

CELLULOSE ACETATE——Vat dyestuffs can safely be applied to cellulose acetate by the sulfoxylate method because of the fact that adequate reduction potentials can be maintained and stabilized at low alkalinities with avoidance of the danger of saponification. The dyestuff is prereduced with a normal quantity of sulfoxylate and with sufficient alkali only to attain complete reduction at a temperature of 180 to 200°F. Application of prereduced dye is made by one of the three following general methods:

1) For light shades—The pH of the reduced dyestuff and of the dyebath is adjusted to a value of 9.5 by addition of acetic acid or monobasic sodium phosphate, and dyeing is carried to completion.

2) For medium shades—In order to obtain better exhaustion, the dyeing is carried out in two stages. In the first stage the procedure is the same as in Method 1 above, that is, the goods are run first at a pH of 9.5 In the second stage the dyebath is further adjusted to a pH range of 6.0 to 7.0, and the dyeing is then carried to completion.

3) For heavy shades—Method 2 above is carried to a third stage. Thus, the goods are run first at pH 9.5, then at 6.0-7.0, and finally in a third stage, alkali is added to raise the pH value to 9.5, at which the dyeing is carried to completion. The addition of 1 to 5% of sodium o-phenylphenate owf is usually necessary to obtain maximum color value, and the addition of this carrier in Methods 1 and 2 above may be necessary in batch applications where expensive dyestuffs are used and maximum exhaustion is desired.

The above three methods are adaptable to either batch-type or continuous application. In continuous application, it is obviously necessary to set up two dyebath units in tandem in Method 2 and three units in Method 3.

The chief problem encountered in application of acid leucos to the various fibers was the maintenance of a stable acid leuco dispersion of small particle size. Many of the dyeings made with the acid leuco were characterized by surface dyeing, probably due to poor dispersion. The various dispersants used were only moderately successful, and practical application is obviously dependent on a solution to this problem.

NYLON——The practice of using sulfoxylate in vat-dyeing nylon is not new, particularly the methods in which it is used in conjunction with hydro. However, in working with the sulfoxylate method it was found that being able to control the pH value of the dyeing was a distinct advantage, particularly where other fibers were involved and where effects or unions were desired. It was also found that dyeings which were superior to both basic and acid hydrosulfite dyeings as well as to basic sulfoxylate dyeings were made by the sulfoxylate vat-acid method.

In this method, the goods are first dyed with the basic sulfoxylate leuco for a short period of time at 180-200°F and the pH is then reduced to a range of 6.0 to 7.0 with acetic acid or monobasic sodium phosphate by converting the basic leuco to the acid leuco on the fiber. The acid sulfoxylate leuco readily exhausts, and the dyeings are most satisfactory.

Since this method for nylon can be used at temperature ranges of 170-190°F, it offers excellent possibilities in the vat dyeing of Helanca, which should not be dyed above 190°F.

DYNEL——The sulfoxylate vat-acid leuco gives excellent results on Dynel when applied by the same procedure as for nylon above, provided 2 to 5% of a swelling agent, such as sodium o-phenylphenate, is included in the dyebath.

DACRON, ORLON 42, ACRILAN CN-33——Full depths on these three fibers at dyeing temperatures of 204-210°F were obtained by the following method of batch application:

In a bath, adjusted to a pH range of 10.5-10.8 with caustic soda and containing the dispersed dyestuff and 5 to 10% of sodium o-phenylphenate ("Dowicide A"), 12 to 20% of sulfoxylate is added. After a first dyeing stage of 10 to 20 minutes, diluted sulfuric acid is added to reduce the pH to 7.0-??, and dyeing is continued for 10 minutes. The third or final stage is accomplished by adding an alkali to raise the pH to 9.5-10.0, during which good exhaustion occurs within 20 to 30 minutes. The goods are rinsed and then oxidized with 2% sodium perborate and 1% acetic acid or with acetic acid and sodium bichromate.

This procedure can be adapted to continuous application by padding the goods at 208-210°F through three dyebath stages, each at one of the three specified pH ranges, respectively, and each containing the carrier and the reduced dyestuff. Optimum conditions of chemical concentration, dyestuff concentration, and immersion time were not determined, but full depths were obtained under practical conditions of concentration and time. The final dyeings were superior to those obtained with hydro or with a combination of hydro and sulfoxylate and thus proved the merit of the sulfoxylate-leuco method.

However, the problem of dispersion was evident, as in cellulose acetate dyeing, and the dyeings showed some surface dyeing defects, though to a much lesser extent.

UNIONS——Sulfoxylate methods offer a valuable tool in the attainment of unions on fabrics or fibers composed of more than one fiber by permitting the various fibers to be dyed at various pH values. As one example, a fiber or fabric composed of a cellulosic type, such as viscose rayon or cotton, and a polyacrylonitrile fiber, such as Dacron, may be colored by dyeing the cellulosic portion at a pH of 11 or above in a first stage, by dyeing in a pH range of 7.0-8.0, and finally dyeing in a third stage at a pH of 9.5 in the presence of sodium o-phenylphenate. Thus, in the second and third stages, the cellulosic fiber has little affinity for the sulfoxylate leuco. This method is adaptable to either batch or continuous application.

OVERDYEING VAT AND AZOIC PATTERNS——A method of overdyeing many vat and azoic effects with vat dyestuffs appears to be promising in that it is less expensive than the use of leuco esters. Three general methods are used, in all of which the dyestuff is prereduced prior to addition to the dyebath:

1) Total caustic soda concentration is maintained at a maximum of 0.20% ows. Dyebath temperature, 160-180°F. Time, 5 to 10 minutes.

2) Normal caustic soda concentration in dyebath. Maximum temperature, 150°F. Time, 5 to 10 minutes.

3) Prereduced dyestuff and dyebath are both adjusted to a pH range of 9.5 to 10.5. Temperature, 160-190°F. Time, 5 to 20 minutes.

In the three methods the reduction potential is thus reduced sufficiently to avoid reduction of the pattern: in the first and third methods by pH control, and in the second method by temperature control. The third method is the most satisfactory, since neither temperature nor time is a critical factor in reducing the color

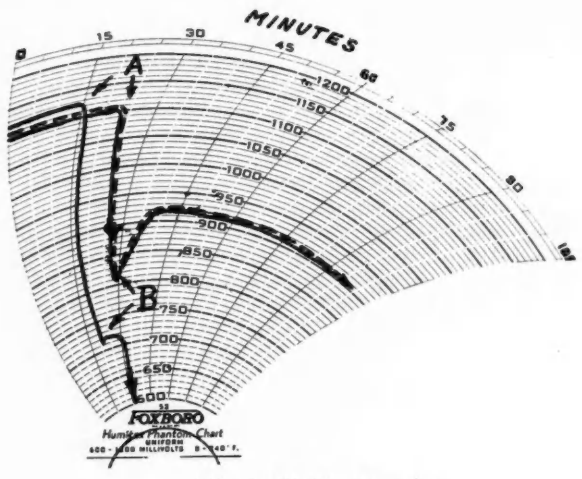
of the effect or pattern. As exhaustion is moderately rapid in all three methods, it is essential in batch-type applications to add the reduced dyestuff slowly. Although most vat colors and azoic combinations are not affected by these methods, some are, particularly azoics; and therefore any pattern should be laboratory tested before carrying out production dyeings.

SPECIAL SIGNIFICANCE OF PH FACTOR———Diserens *(20)* states that two general theories are postulated for the constitution of sodium sulfoxylate formaldehyde, one proposing the formation of an ester of sulfoxylic acid and the other, a derivative of hyposulfurous acid. In either case acidic products of decomposition are formed *(15)*, but our experiments show that the acidity of the bath from decomposition of the sulfoxylate is not as high as the acidic sodium bisulfite formed *(1)* by the decomposition of hydrosulfite (which is officially called hyposulfurous acid by the ACS). Brearley *et al (22)* assert that sodium sulfoxylate-formaldehyde solution is stable to the action of acids down to a pH of 3. Our observations made on blank vats with sulfoxylate versus hydro in which redox potentials were studied at varying pH values showed clearly the superior stability of sulfoxylate at low pH values. The superior stability of sulfoxylate compared with hydrosulfite in an acid medium is graphically illustrated in Figure 7, in which the effect of lowering the pH on the redox potential at 200°F is seen. In Figure 7 an equivalent pH is reached with hydro upon the addition of half as much acid as compared with sulfoxylate.

Initial reduction of redox potential is greater with hydro at the same pH, and, while the potential of the sulfoxylate is well stabilized at a desirable value, the potential of the acidified hydro remains stable only for a few minutes and then takes a rapid drop out of the desired range, similar to the drop which is characteristic of normal alkaline hydrosulfite leuco baths when permitted to go out of reduction. Under this latter condition it is possible that the increased stability of the sulfoxylate reduction bath is due to the evolution of decomposition products of lower acidity compared with hydrosulfite.

Revisions of data contained in Table III must be made in the light of the late observations in which critical pH ranges were determined to be significant in improving absorption and affinity of those dyestuffs which did not exhibit satisfactory affinity on cotton in sulfoxylate-leuco systems. This improvement could be attributed to the influence of the pH factor on the absorption of the fiber, or to the increase in affinity of the leuco, or to both factors.

REDUCTION POTENTIAL IN MILLIVOLTS VS TIME AT CONSTANT TEMPERATURE (200° F)



——— Sulfoxylate-NaOH 0.5 oz/gal
———— Hydrosulfite-NaOH 0.5 oz/gal
A—Addition of acetic acid
B—pH value of 6.0 (by indicator paper)

Figure 7

Effect of lowering pH on reduction potential

The data were insufficient to be incorporated in this study as a complete tabulation, but an example may be given in the behavior of Anth Vat Copper Brown, a dye which is known to be unstable at elevated temperatures in normal hydrosulfite reduction. This dyestuff exhibited superior stability and color value on cotton when dyed at 180°F at reduced pH value (10.5-11.5) after initial alkaline reduction and dyeing at 200°F.

THEORETICAL

During our work we encountered significant differences in the appearance, properties, and behavior of the sulfoxylate leucos as compared with the normal alkaline hydrosulfite leucos. These phenomena may be explained by several possible general hypotheses: by the existence of a resonance relationship of the same specific leuco, by the existence of a different leuco, or by the occurrence of molecular rearrangement. These conditions seem indicated as possibilitjes by observed variations in the leuco colors from the known colors of the normal leucos, as well as by observed variations in the affinities of the leucos.

The difference in properties could be due to the formation of a leuco in which the stress is on a different form of the possible resonance in the leuco. Semiquinone formation can be indicated by intermediate color changes *(13)* as reduction progresses. This has been particularly noted in our experimental dyeings, and the color change might indicate the possibility of the formation of one or more of the semiquinones.

The statement of Clibbens *(16)*, that normal reduction of the indanthrones produces only the dihydro derivative, but that in all the other groups or families all the keto groups are normally reduced, is generally accepted *(1, 13)*. There are two strong indications that, in sulfoxylate reduction, a lesser number of keto groups is reduced than in normal hydro reduction. First, in the reduction of the indanthrones, there was no indication of formation of the tetrahydro derivative, even under extreme conditions, as opposed to noticeable formation with hydro, and, secondly, with other anthraquinone derivatives there appeared to be a reduction in affinity of some of the dyes which contained large numbers of keto groups. Anthraquinone Vat Khaki 2G (Pr 122), the molecule of which contains ten keto groups, was a good example.

The possibility of a stronger susceptibility to molecular rearrangement must also be considered, since Khaki 2G is very subject to this phenomenon *(1)*. This possibility might also be indicated by the fact that Indanthrene Turquoise Blue 3GK, which contains three keto groups, appears to be as easily overreduced with alkaline sulfoxylate, as with alkaline hydro, an occurrence not noted with other dyestuffs containing halogen and amino groups in similar positions. This was the only instance of decreased leuco stability with sulfoxylate in the experiments. It has therefore not been indicated by the experiments that overreduction can

not take place in sulfoxylate-leuco systems; but, it is evident that their resistance is greater for the majority of dyestuffs than in hydro-leuco systems. As an example, very low concentrations of the leucos of the halogenated indanthrones (less than 0.005% ows) were subject to gross excesses of NaOH and sulfoxylate reducing-agent concentrations at 208-210°F at extremely high reduction potentials (over 1250 millivolts) with no stabilizing materials added for over one hour with only slight loss in color value, as shown by the oxidized dyeing.

The hypothesis can possibly be evaluated by polarographic and spectrophotometric studies, which are anticipated as a future project. It was hoped in the initial preparation for this study to be able to correlate known leuco potentials of many of the dyestuff studies with chemical structure and to correlate further positive and negative features of sulfoxylate reduction with both known leuco potentials and with the chemical constitution of individual dyestuffs and group classifications. As the experimental work progressed, it became apparent that there was no valuable correlation with various published leuco potentials other than the obvious fact that dyestuffs of lowest leuco potentials were more easily and quickly reduced with sulfoxylate. It is felt that some of the experimental findings in this study will serve as a primary guide to further the study of correlation with chemical structure as pertaining to the reduction action of sulfoxylate, and it is further anticipated that such a study might result in being able to predict the extent and nature of the reactions for individual dyestuffs.

An attempt to evaluate those dyestuffs which appear to be moderate in the affinity of their sulfoxylate leucos for cotton brought no immediate conclusion. It is to be emphasized that dyeing conditions for dyestuffs as tabulated are average near-optimum conditions based on experiments thus far and are not to be considered as optimum for specific conditions. In the examples of production dyeings, the conditions are merely optimum thus far, but are near enough to theoretical optimum to offer substantial practical advantages. It is recognized that additional evaluations of individual dyestuffs under varying conditions must be made. The oxidation factor, which could not be fully considered in this study, is perhaps of special importance, since affinity of the leuco could be insufficient to prevent a substantial quantity of dyestuff being lost before oxidation is carried out.

The phenomenon, discussed in other sections, pertaining to the influence of the pH factor on sulfoxylate leucos could perhaps be important in arriving at a satisfactory theoretical explanation for the behavior of sulfoxylate leucos in general. The possibility that the behavior is simply a function of absorptive capacity of the fibers cannot be overlooked, but it appears more likely that the behavior variations from the normal hydrosulfite leucos are induced by physical or chemical properties of the leuco forms. The sodium salt of a normal hydrosulfite leuco compound is the salt of a weak acid and a strong base, and the equilibrium would tend towards the direction of the hydroloyzed leuco, unless a large excess of strong alkali is present *(1)*. This equilibrium relationship can be assumed to be similar in sulfoxylate reduction, but perhaps with a more stabilized tendency toward the direction of the sodium salt of the leuco because of the less acidic decomposition products of the sulfoxylate. Since the equilibrium relationship is apt to be more stabilized at low or intermediate pH values, there would appear to be a possibility of the existence of a stabilized conglomeration of three leuco forms: the sodium salt, the acid, and a third or intermediate form, the molecules containing some hydrolyzed keto groups and some enolated keto groups. Thus the "intermediate" hydrolyzed leuco, mentioned frequently herein, might be a mixture of the leucos of a single compound of different molecular constitution. The affinity and absorption variations of the sulfoxylate leuco might also be possibly attributed to an hydrotropic effect of the decomposition products of sulfoxylate.

SUMMARY

Reduction potentials obtained with sulfoxylate were comparable to those obtained with hydro, indicating the development of potentials beginning at temperatures of 160°F and upwards sufficient to accomplish satisfactory dyeings. The behavior of many vat dyestuffs in sulfoxylate reduction indicated a desirable slowed reduction and exhaustion, particularly in batch-type operations. Excellent production dyeings were made on cotton yarn in package form with sulfoxylate both without hydro and in conjunction with hydro. An evaluation of vat dyestuffs on mercerized and unmercerized cotton disclosed that, although the quality of the dyeings was improved because of slower exhaustion rates, many of the leucos did not possess enough affinity for the fiber to give color values comparable to the hydro controls. In most cases this disadvantage could be obviated by the use of a small quantity of hydro at the end of the dyeing cycle.

The stability of the indanthrones was found to be improved at high temperatures by the use of sulfoxylate as the reducing agent, and there were indications that other groups were similarly affected to a lesser extent. The advantages of higher application temperatures are well-known for cellulosics *(16)*, as well as for noncellulosics. The experimental work in continuous applications was not sufficiently complete to make specific recommendations, but observed low "strike," minimized differential exhaustion of dyes used in combination, and high-temperature stability indicate good possibilities for any applications. Experimental dyeings on viscose rayon indicated promising possibilities particularly because of the easier control of the rate of exhaustion and the pH of the dyebath. The use of sulfoxylate leucos also permits high application as well as high reduction temperatures with minimized instability of some of the unstable dyestuffs.

There is one precaution which must be taken and which cannot be overemphasized if success is to be achieved by any of the prescribed methods with sulfoxylate. In pigment application, well-dispersed dyes must be used, the dispersion must remain stable, and great care must be exercised to prevent agglomeration before reduction occurs. If agglomeration does occur, particularly in heavy shades, the dyeing will be spotty but can be corrected by rereduction with hydrosulfite better than with sulfoxylate. This must be considered a disadvantage of the sulfoxylate method in that it is somewhat more critical than with hydro. Low titer soap appears to be the dispersing agent that minimizes agglomeration difficulties.

In the production of acid leucos, sulfoxylate appeared to offer advantages over hydro in that pH control was easier and the acid vat was more stable in high temperature applications. A practical method of overdyeing vat and azoic effect fabrics was found in which the sulfoxylate reduction bath, under proper conditions, does not affect the underlying pattern. By a variation of the same method, vat redye additions can be made very simply without any loss in the color of the original vat dyeing.

Tests on the fastness of the sulfoxylate dyeings did not disclose any depreciation, as compared with the normal listed ratings of individual dyestuffs, because of any inherent properties of the dyes or the fiber, and, when any loss of fastness was noted it was attributed to other factors which are normally causes of such losses.

It must be emphasized that the results contained in this paper should be considered only as a progress report on the investigation of the subject, which developed more broadly in scope than was anticipated, preventing a complete study of all possible phases. One important aspect of this study which would be invaluable, but which was not possible to complete in the time allotted, was the spectrophotometric analysis of the leucos

obtained and correlation of this data with the other significant factors in the reduction and dyeing cycles, such as the redox potentials. Such an analysis, as described by Royer *(17)*, is anticipated in connection with a future investigation.

CONCLUSION

The use of sulfoxylate as the primary reducing agent in vat dyeing offers advantages in applications where any of the following factors are desired:

Slow rate of exhaustion.

Controlled rate of exhaustion.

Controlled "strike".

Dyestuff stability at elevated temperatures.

Stability of reducing agent at elevated temperatures.

Control of pH factor during reduction and dyeing.

The principal disadvantage found in the new application method was the difficulty in determining the optimum application conditions for the leucos of some of the dyestuffs, which displayed reduced affinity, particularly for cotton, under the conditions tried thus far and which therefore gave less color value than when applied as a hydrosulfite leuco from an alkaline solution.

The practical applications suggested for the sulfoxylate method are as follows:

a) To obtain full shades on hydrophobic synthetic fibers on existing equipment without high pressure.

b) For improved quality on yarn dyed in circulating machines.

c) For dyeing of knitted or woven goods in batch applications where penetration is a problem.

d) For high-temperature continuous dyeing where stability of dyestuffs is a problem.

ACKNOWLEDGMENT

We wish to acknowledge the co-operation of the following companies in furnishing helpful information, material, and data used in the presentation of this paper:

American Aniline Products, Inc
Dyestuff Department, American Cyanamid Co
Ciba Company, Inc
E I DuPont de Nemours & Co, Inc
The Foxboro Company
General Dyestuff Corp
Macbeth Corporation
National Aniline Division, Allied Chemical and Dye Corp
Royce Chemical Company

NOTE: It is regretted that the black-and-white photographs of the dyeings, especially in the yellow, orange, and red ranges, and in Figures 4 and 5, do not clearly indicate the gradations in depth of shade of the comparative dyeings. However, the differences could be seen more clearly in the colored slides and in the actual dyeings which were on exhibit at the Intersectional Contest booth. In the photograph of Figure 5, the extreme right hand column S_n is misleading, since the actual dyeings are equal or heavier in depth than the column H_n.

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192nd Council Meeting——

(Concluded from page P524)

JUNIOR

C A DiPippo — R C Lakey
G L Frericks — H J Morton
R E Iannone — V S Ryan
A J Trentesaux

ASSOCIATE

R J Asbill — R C Hasenclever
J E Barbre — E J Jennings
J W Burch — J J McMahon
R Chisholm — N A Mignone
W J Goodwin — W A Raczynski
R Safioen

STUDENT

P G Carlson, Jr — G R Norwood
C K Cobb, Jr — R E Rondeau
S Deckelbaum — D M Rubin
N J Geary — R C Schiek
E H Jackson — H N Tobler

Transferred from other classifications to Senior

S Amodei — M E S Metze
H H Bander — R E Sebra
A W Cowan — R N Armour
E Holt — J Cosgrove
J A McGuigan — A J Berube

Respectfully submitted
H C CHAPIN
Secretary

EMPLOYMENT REGISTER

This column is open for two insertions per year, per member, without charge. Blanks can be obtained from, and filed with, the Secretary of the Association, Lowell Technological Institute, Lowell, Mass. It is understood that these will be open to inspection by prospective employers who can obtain further information from the Secretary.

54-17

Education: BTC, Lowell Tech Inst.

Experience: Chemist and dyer, hosiery and synthetics.

Age: 49; married; references; New England preferred, but will go elsewhere.

7-16, 7-30

Membership Applications

SENIOR

James F Davis—Dyer, Goodwill Mfg Co, Flomaton, Ala. Sponsors: W W Bussey, E V Helms.

William P Dooley—Development Service Dept head, American Viscose Corp, Nitro, W Va. Sponsors: J C Woodruff, L L Walmsley.

George C Murphy — Colorist — quality control, National Aniline Div, Allied Chem & Dye Corp, Chesterfield Plant—Fiber Division, Hopewell, Va. Sponsors: H C Chapin, E E Fickett.

Jorge J Pagani—Head dyer of Sudamtex de Uruguay S A, Solonia, Uruguay. Sponsors: C Z Draves, H Halvorsen.

Eric Silvers—Agent of General Dyestuff Corp, New York, Milan, Italy. Sponsors G G Neisser, H E Hager.

JUNIOR

Edmond C Campbell, Jr—Salesman, Roma Chemical Corp, Brooklyn, N Y. Sponsors: C M Christiansen, S Wood.

ASSOCIATE

Juan A Masso—Sales Technical Section, R Masso & Cia, Barcelona, Spain.

APPLICATION FOR TRANSFER TO SENIOR MEMBERSHIP

John F Cobianchi — Walter E Kramer
George H Fisk — Cesar Manevich
Moises Haimchick — George S Y Poon
Eric O Herzog — Ruedi E Weber
Daniel W Young, Jr

ACTIVITIES OF THE LOCAL SECTIONS

Piedmont Section

THE 1954 Summer Outing of the Piedmont Section was held June 11 and 12 at the Mayview Manor, Blowing Rock, N C with approximately 320 members and guests attending.

Friday night a "Millionaires' Party" was held with the first prize going to Henry Gaede of the Laurel Soap Manufacturing Company. This party was followed by an informal dance in the ballroom.

Ideal weather on Saturday encouraged participation in the golf, shuffleboard, and horseshoe-pitching tournaments. Gordon Eaves of the Cloverdale Dye Works, Inc, won top honors in the golf tournament with a low gross of 75 on the par 71 Blowing Rock course.

Winners of the horseshoe-pitching tournament were Lee Tigler of the Kerr Finishing & Bleaching Works, and R P Anthony of Seydel-Wooley & Co. First prize in the shuffleboard contest went to M G Morris of the National Aniline Div, with James E Greer of Burlington Mills Corp winning second prize.

Joe McDowell of F H Ross & Co and Robert Ward of Leaksville Woolen Mills, Inc, shared putting honors on the 9-hole putting green at the Manor.

In the women's flight Mrs Ira Hurd had a low gross of 85 and Mrs Reid Tull, a low net of 79.

A cocktail hour preceded the banquet in the Main Dining Room of the Manor on Saturday.

Warren E Rixon, Carbide & Carbon Chemical Co, served as Outing Chairman. He was assisted by James Balloch, Jacques Wolf & Co; G Meares Randolph, Moreland Chemical Co; Richard E Rettew, Southern Polymer, Inc; John G Sibley, Jefferson Chemical Co; Harry L Welsted, Jr, Monsanto Chemical Co; J Bracken Johnson, Virginia Smelting Co; and Earl Holt, Bryant Chemical Co.

—◆ ◆—

Southeastern

CRUSSELL GILL, Southern Sizing Co, took low gross honors in golf as the Southeastern Section met for its annual outing at Radium Springs, Ga on May 14-15, while Wayne Hays, Callaway Mills, led the field in horseshoe-pitching. Other golf winners included Bill Pearson, Hilton-Davis Chem Co (low net, salesmen) and Val Winkleman, Russell Mfg Co. (low gross, millmen).

Jack Boykin, National Aniline Division, served as general chairman for the affair, with Bob Hallowell, Coats & Clark, handling the golf tournament. The bridge tournament was strictly a "ladies only" competition.

Western New York

THE officers of the Western New York Section held their first meeting on July 8, 1954 at National Gypsum Research Laboratories. Plans to launch the initial season were discussed and meeting dates set, as follows: October 8 (Buffalo), November 27 (Hamilton, Ontario — in conjunction with the CATCC meeting), January 14 (Buffalo), March 4 (Hamilton, Ont with the CATCC), April 22 (Buffalo), June 24 (Outing).

Committee Chairmen appointed by Chairman J G Kern are as follows:

Speakers Program—Kelvin H Ferber
Intersectional Contest Paper—F Vincent Mahoney
Membership—Robert A Hoffman; Robert H Burrows (Ontario), *cochairman*
Publicity—Margaret R Hallinan
Dining—Kelvin H Ferber
Sectional Research—Berne L Woolley.

—◆ ◆—

Pacific Southwest

TWENTY-ONE members were present for the regular quarterly meeting of the Pacific Southwest Section on June 4 at the Gourmet Restaurant, Beverly Hills, Calif.

During the business meeting, Sidney Springer, chairman, reported that Charles Dunker, former treasurer of the Section, had passed away.

The following were named to serve on the Nominating Committee: Paul Noonan, Leon Olson, and Serge Dadone, *chairman*. A motion that Clarice Lindsay be retained as secretary was carried.

Theodore Smock, program chairman, introduced the speaker of the evening, Kenneth Kendal, Beckman Instruments Division, who discussed and demonstrated the company's Model DR recording spectrophotometer.

The Section will hold its outing on October 30th at Ojai, Calif, and the next quarterly meeting has been set for November.

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Philadelphia

PAPERS on the solution dyeing of acetate and rayon will be presented at the next regular dinner meeting of the Philadelphia Section on September 24, at the Penn-Sherwood Hotel, 39th and Chestnut Streets, Philadelphia, Pa.

A Frank Tesi, Celanese Corporation of America, will speak on the "Solution Dyeing of Acetate" and will share the program with L Leslie Walmsley, American Viscose Corporation, speaking on "Solution Dyeing of Rayon."

Northern New England

THE 29th Annual Outing of the Northern New England Section was held at the Merrimack Valley Country Club, Methuen, Mass on June 11, 1954.

John P Ploubides, Pacific Mills, was chairman of the Outing Committee, which consisted of the following:

Chairman Ex-Officio—Ernest R Kaswell, Fabric Research Labs
Softball — Joseph E Travers, United Aniline Co
Golf—Joseph A Bryant, Bryant Chemical Co; Wm A Schmottlach, Goodall-Sanford, Inc; John Ormiston, Sandoz Chemical Works, Inc; Julius Jarek, Verney Corp
Horseshoes — Henry Rooney, Pacific Mills
Dining—Edward B Bell, Textile Aniline & Chem Co; John R Markgren, W C Durfee Co, Inc
Prizes—M Lane, Geigy Co, Inc; Chester Brown, Geigy Co, Inc
Program — Azel W Mack, Dexter Chemical Corp; John F Sheehy, Pacific Mills
Publicity—E M Lynch, Jr, The Derby Co, Inc; F J O'Neil, Pacific Mills
Finance—Chester Kopatch, Ciba Co, Inc; Phil Graham, American Cyanamid Co
Music — Harold Kaswell, Fabric Research Labs.

Low gross honors in the Class "A" golf tournament went to Andrew Gard, Versenes Inc, with a 77. Walter Wood, National Aniline Div, was second with a gross of 78.

Winners in the guest division were Joseph Finn, low gross and William Deminie, low net. Alfred Gavin won the prize for being nearest the pin on the 16th hole. Julius Jarek, Verney Corp, had the longest drive on the 15th hole. Warren Dewing, General Dyestuff Corp, won the putting contest.

In softball, a team captained by Herbert Wilkinson, American Aniline Products, Inc, defeated a team captained by Alan Burke, Metal Fabricators Co.

Horseshoe singles honors were won by Richard Herrick, United Aniline Company. Doubles were won by Earl Bullard, Charlton Woolen Co, and H E Glidden, Lowell Technological Institute.

—◆ ◆—

Mid-West

CFRED GURNHAM currently heads the Mid-West Section's Committee on Stream Pollution, which was formed in 1952. Other members include R C Anderson, Lee G Johnston, James Crane, and F Harry Proudfoot.

Mid-West Section Outing Features Millmen Victory in Softball

WITH an assist from the weatherman, the Mid-West Section held its annual outing June 12-13 at Lake Lawn Lodge, Delavan, Wis, under ideal conditions; and with an assist from mortal sources (other than the players for the most part), the Millmen administered their annual softball trouncing to the Peddlers 9 to 6.

The line score:

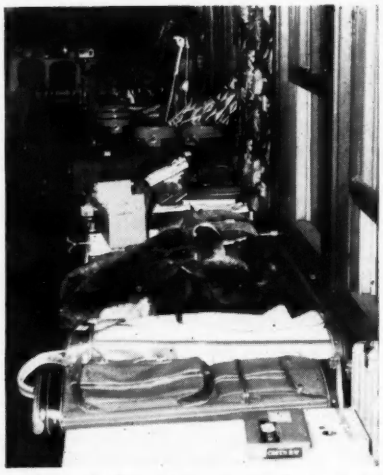
						R	H	E
Millmen	1	1	2	1	4	9	14	0
Peddlers	4	2	0	0	0	6	15	2

Official statistics indicate that the Millmen, headed by co-captains W Fischer, Milwaukee Dyeing & Bleaching Co, and A Blackburn, Western Felt Works, played errorless ball in defeating the Peddlers, headed by co-captains W Paine, General Dyestuff, and A Coleman, Victor Chemical. Jim McGowan, Morgan Dye & Bleach, and Clarence Wille, Burson Knitting, handled the umpiring chores.

Photos of this epic struggle appear on page P544.

Golfing activities began on Friday afternoon with a 2-ball foursome, selective-drive tournament. First prize went to J H Jones, Phoenix Dye Works, and A I Hultberg, Bear Brand Hosiery; 2nd prize, to J J Bernard, Rohm & Haas Co, and C A Whitehead, American Dyestuff Reporter; and 3rd prize, to J C Finley, Paramount Machine Co, and D G Brown, Strutwear Knitting Co.

(Concluded on page P544)



A few of the prizes awarded to lucky winners

HEAD TABLE

(L to r): V Braun, Aluminum Extrusion Corp, Outing Committee; L Voss, Geigy, Sectional Committee; J H Jones, Phoenix Dye Works, national vice president; A I Hultberg, Bear Brand Hosiery, vice chairman; J G Stott, chairman

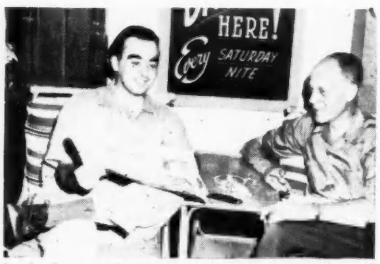
National vice president J H Jones "gets the thumb" from umpire J L McGowan during the heat of the Millmen-Peddlers softball game

(L to r): F E Schroeder, Prospect Chemical, outing chairman; H Ericson, American Aniline, secretary; J G Kelley, DuPont, treasurer; J M Remsen, Du Pont, Outing Committee; W D Paine, General Dyestuff, Outing Committee

Low gross winners J M Remsen, DuPont (member), left, and F Snyder, Copeland-Milne Wool Co (guest)

Laurence E Schall, Textileather (left) and Elmer Scharf, L Sonneborn Sons

(L to r): H Faurot; Herman Boxser, Acadia Synthetic Products Div; D Anderson, Phoenix Trimming; Allen Kidder, Western Felt Works

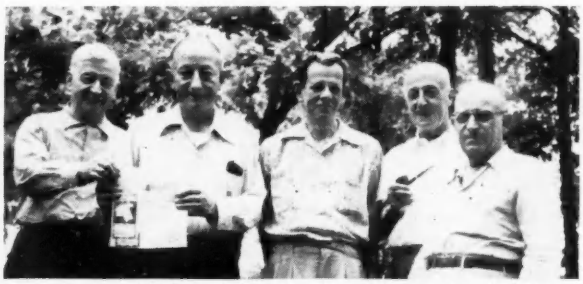


J J Bernard, Rohm & Haas (left); C Hughson, Chicago Printed String

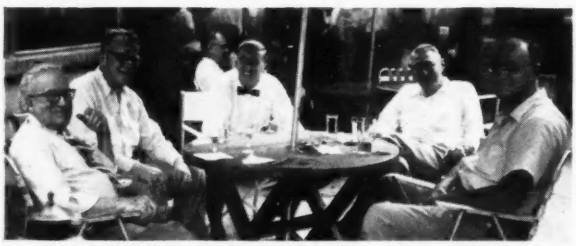
Seated (l to r): Eric Camp, National Aniline; Sam Klein, Am Cyanamid; A I Hultberg, Bear Brand Hosiery
Standing: Bill Fisher, Milwaukee D & B; Bill Paine, General Dyestuff

At the horseshoe pits
Identified are Axel Olsen and B Isenogle of Aurora Bleachery (2nd and 3rd from left)

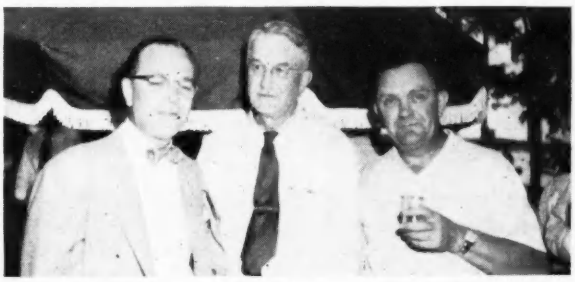
Sweet Adeline?
(L to r): H Lofghren; "Babe" Degryse and J L McGowan, Morgan Dye & Bleach; Frank Hartman, Phoenix Hosiery



(L to r): John Noble and Fred Scholler, Scholler Bros; H Ericson, American Aniline; Ted Atkinson; L B MacFarland, American Aniline



(L to r): H Proudfoot, Nyanza Color & Chem; G R Kremers, Strutwear Inc; unidentified; B F Marthens, American Soap & Chemical



(L to r): Frank Myers, Geigy; Ellis Gurry, Aurora Bleachery; W C Snead, Textileather

Tea time

Mid-West Outing——

(Concluded from page P542)

Saturday's golf resulted in the following winners:

Low gross (members)——J E Remsen, Du Pont——78

Low gross (guests)——F Snyder, Copeland Milnes——77

Closest to the pin——D G Brown, Strutwear Knitting

Longest drive —— C Kurowski, Midwest Processors

Class "A" hdcp——A I Hultberg, Bear Brand Hosiery, 70-19-61; G Willgeroth, Chemical Products Co, 80-15-65; A Rathke, Contour Hosiery Mills, 83-18-65

Class "B" hdcp——S Brainerd, Rollins Hosiery Mills, 95-36-59; J Eich, General Dyestuff Co, 94-33-61; F Connelly, Morgan Dyeing and Bleaching, 83-18-65

Class "C" hdcp —— R Carr, Geigy; 105-54-58; H Calvert, Western Felt Co, 106-48-58; F Gorsky, Morgan Dyeing and Bleaching, 107-48-59

Class "D" hdcp——E Hazecamp, General Dyestuff, 124-69-55; R Teal, Western Piece Dyers & Finishers, 127-72-55; F Acker, National Aniline, 138-78-60

In the horseshoes competition, Bernard Isenogle, Aurora Bleachery, reigned supreme in the singles, and the team of F Davis, Prim Hosiery, and G Fauby, Maher Color & Chemical, took the doubles championship.

H Jayr, National Printed String, and E Scharf, L Sonneborn & Sons, defeated all comers in shuffleboard.

One hundred forty eight guests were present for the affair, which was under the chairmanship of F E Schroeder, Prospect Chem Co, and the following Committee members: V Braun, F Beverly, K Harms, E Hazekamp, J Jones, J Kelley, J Remsen, and C Sillin.

MILLMEN 9 — PEDDLERS 6

Abstracts——

(Continued from page 520)

cessed into yarns and fabrics.

Among the various fabric characteristics examined were strength, abrasion resistance, wrinkle recovery, crease retention, flammability, and sensitivity to humidity, dycleaning, and laundering. The results of these tests are presented in tabular form.

In general, Dacron polyester fiber in combination with wool, acetate, or rayon increased fabric strength, abrasion resistance, press retention, wrinkle recovery, and stability to changes in relative humidity when compared with 100 percent wool, acetate, or rayon fabrics. Orlon acrylic fiber increased fabric strength when blended with wool and acetate. Blends of Orlon with rayon, wool, or acetate showed increases over fabric of the appropriate older fiber in stability to drycleaning, laundering, and humidity changes, and in ability to retain pressed creases. Abrasion resistance and crease recovery at normal and high humidities were increased by Orlon when blended with rayon or acetate. Nylon contributed substantially to increased abrasion resistance in blends with wool, rayon, cotton, or acetate. Stability to changes in relative humidity was improved by nylon added to rayon and acetate.

Twelve references to the literature are cited.—WHC

Synthetic Fibers in Combination Fabrics

H C Mersereau, *Canadian Textile J* 71, 53-5, April 23, 1954.

The author point out that true homogeneous fiber blends are rather unusual in the industrial field. "Combination" fabrics (e g, continuous filament nylon in the warp and spun viscose in the filling) are quite common and extremely versatile.

The reason for using a particular fiber in an industrial application is usually to obtain some particular physical property, such as strength, chemical resistance, or abrasion resistance. A homogeneous blend of two fibers will normally be only as valuable as the poorer component. The tendency, therefore, is to use 100 percent of the best available fiber. There are exceptions, however.

The use of wool in a well-milled woven fabric, erroneously called a "felt," to support the wet sheet in the manufacture of paper is well known. This fabric has to stand up to very severe conditions of usage, including high speeds, high pressures at the nip, and exposure to bacterial degradation. A blend of 15 to 20 percent of nylon in the filling threads is said to more than double the life of the felt in some cases.

Similarly, in cotton chafer fabrics for automobile tires, a blend of 15 percent nylon with the cotton in both warp and filling considerably increases the abrasion resistance.

The use of blends of from 25 to 50 percent nylon staple with viscose rayon has become increasingly common in certain automobile upholstery fabrics. Also in carpets, blends of 10 to 20 percent nylon with viscose produce a pile with substantially improved wearing properties.

Attempts to increase the strength of cotton duck used for belting by blending with nylon were not successful unless over 50 percent of nylon was used. More success was obtained by combining continuous filament nylon with 100 percent cotton yarn in the warp threads.

Fire hoses have recently been designed with a nylon circular filling combined with a cotton warp. This improves the flexibility and reduces the weight. Hose made from a polyester fiber for the filling and nylon for the warp has also been made experimentally; this is even lighter and avoids the danger of mildew.

A combination nylon warp and fine combed cotton filling for lightweight tents was used in the recent Mount Everest expedition. The nylon provided lightness and abrasion reseistance, while the cotton filling permitted a certain amount of water vapor to penetrate the fabric for comfort purposes, but would swell when wetted by rain to give a waterproof fabric.

A braided cord for television aerial supports is described. A nylon core provides strength, and a braided Orlon covering provides sunlight resistance. This construction is much lighter than metal wires, and results in less electrical disturbances, since both fibers are nonconductors.—WHC

An Introduction to Continuous Dyeing

A S Fern, *Textile Recorder* 72, 101, May, 1954.

Uniform impregnation and fixation are the two basic principles of continuous dyeing with vat dyes on cellulose. The impregnation is best accomplished under conditions of low substantivity (i e, by pigment padding), but the fixation should be effected at high temperature, so that no migration of the dye takes place when it is reduced and becomes substantive.

The main features of an ideal continuous vat dyeing system, according to the speaker, are economy of processing (chemicals, heat, and labor), ease of changing shade, large outputs handled at high speed, and small lot-handled economically, quality as good as by batch methods, handling of a wide variety of fabrics in depths of shade, the shade not affected by the running speed, no opportunity for dye decomposition, and accurate laboratory shade matching.

The continuous process has certain limitations. The dyes used must have high-temperature stability and must be finely dispersed, if applied in pigment form. Fibers of low wet strength can rarely be processed continuously; knit fabrics are readily distorted; stiff fabrics may crack; while pile fabrics cannot be heavily squeezed. Also dead cotton is sometimes poorly covered.

Referring to equipment now in use for continuous dyeing the speaker mentioned the Williams unit (with reduced volume of liquor and high turbulence), the Bond machine (which also employs turbulence and mechanical squeezing to assist penetration), the pad-steam process, and the Standfast molten-metal technique.

He described the so-called "Krahenbuhl" system of dyeing wool, in which the fabric is padded with acid dyes and acid-boiled continuously. The molten-metal process has also been used experimentally in dyeing wool, he said. He also mentioned the possibility of continuous dyeing of acetate, nylon, and Terylene.—WHC

Affinity Effects During Padding

W J Marshall, *Dyer* 111, 654, April 30, 1954.

The ideal continuous dyeing system consists of a stage of purely mechanical application of the dye without affinity, followed by rapid fixation *in situ*. In practice this ideal system is difficult to achieve, but the "pad-steam" method of dyeing vat dyes, where a pigment pad is followed by a chemical pad and steam fixation, approaches this ideal closely. Even here, however, bleeding-off of the pigment pad liquor into the chemical pad is a source of "tailing," and in practice this is overcome by adding to the chemical pad and arbitrary proportion of the pigment-padding liquor.

This technique is probably the best method of covering irregularities in spun rayon fabrics introduced by weaving variations, because the mechanical impregnation ensures that each portion of the cloth receives only its quota of dye.

If in the pad-steam process the pigment-padded cloth is not dried before entering the chemical pad, the reducing bath becomes diluted, and a higher concentration of hydrosulfite and caustic in the feed-liquor is necessary to maintain equilibrium.

In the case of padding direct and leuco vat dyes, owing to the affinity of the dye for the fabric, the dye is absorbed by the cloth more rapidly than the dye-liquor.

As a result, the concentration of dye in the liquor gradually drops, causing a variation in shade. The drop in concentration will vary with different dyes, depending on the "affinity factor" of each dye.

To avoid this, there must be a precise balance between the amount of each dye fed into the padding mangle and the amount of dye leaving it. A small padding trough is a definite advantage here. Success in padding these dyes depends largely on the skill of the dyer in making the necessary adjustments.—WHC

Use of Nylon Yarns in Fish Netting

E R Needham, *Canadian Textile J* 70, 74-6, October 9, 1953.

In the course of the past few years, nylon has assumed an increasingly important role in the fish netting industry, being used both in the nets themselves and in the heavier cordage employed in rigging and hanging the net. While staple nylon has found uses in certain applications, by far the most spectacular development has been in the use of filament nylon.

Perhaps the fiber's outstanding attribute is its high strength; with a single exception, nylon is stronger than any of the commonly used natural fibers. Of the man-made fibers, very few can lay claim to being stronger than nylon, and of these none has been commercially adapted to netting. Two things tend to spoil the chances of using nylon's strength to full advantage: the first is that it loses strength when wet, and the second is that the strength of the twine when knotted shows an important drop below the straight twine strength.

Toughness, as measured by the ability to absorb work, is especially significant in the netting field, where strains are likely to be shock loads. Nylon's great toughness is to a large degree derived from its high elongation possibilities; thus it is "tailor-made" to withstand the rapid shocks encountered in the field.

Nylon's resistance to attack by microorganisms is well known, and it is obvious that this is a great benefit in netting. Probably the greatest cause of strength loss of natural fiber netting in use is due to attack by cellulose-digesting bacteria found in sea and fresh water. Nylon is virtually unaffected by the common molds (e g, *Chaetomium globosum*), and this, too, is a decided advantage. Quite often netting is destroyed by mildew when it is stored damp or in moisture-laden locations. Thus nylon is easier to store, since it does not have to be carefully dried beforehand.

Nylon's hydrophobic tendency is a great advantage to the fisherman. Nets take less time to dry, and are therefore easier to store. Lower water pickup means less weight when the net is hauled into the boat.

Nylon is known to possess outstanding abrasion resistance, and this serves it in good stead in the everyday wear and tear of fishing.

In common with other textile materials, nylon is degraded by the action of light, especially the blue and violet components of sunlight. In this respect, bright nylon is much better than the delustered type. It is therefore very important to avoid direct sunlight in drying of nylon netting.—WHC

• PATENT DIGEST •

PAUL WENGRAF

WATER-REPELLENT TEXTILES Treated with Silicone Oil Emulsions G, 2, 02

(U S Pat 2,662,039)
(Harris Research Labs——Brown, Sookne, Minor——Dec 8, 1953)

This application has been derived from the application for US Pat 2,597,614 [cf *Am Dyestuff Reptr 42,* 18 (1953)], which refers to water-repellent finishing emulsions based on silicone oils. These emulsions are prepared by dissolving monomethyldichlorosilane in an appropriate organic solvent (benzene) and then stirring this solution with water to which an emulsifier of the "Igepon T" class has been added. It is suggested that dilute solutions be employed in order to avoid the formation of highly polymerized silicones.

The main modification of this procedure, as protected by the current patent, appears to be the addition of a diluent to the inert solvent for monomethyldichlorosilane. Dimethyldichlorosilane, which is very active chemically, is preferable. Additions in the ratio of one part of dichloro product up to two parts of monochloro product will retard polymerization for a longer period.

Example (#4): Three parts by volume of dimethyldichlorosilane and four parts by volume of the monochloro product are dissolved and added to the aqueous slurry of sodium acetate trihydrate and the above-mentioned emulsifier. A poplin fabric is made water repellent by immersing it in the dilute emulsion, which exhausts in a short time, drying at room temperature, washing, drying again, and curing for two hours at 110°C. (From this example it may be concluded that the emulsion is highly substantive to the fiber.)

A delay of polymerization may also be effected (and the amount of dichlorodimethyl silane reduced) by cooling the reaction mixture during hydrolysis. It has been observed that the rate at which the organosilanes are added to the aqueous solution must not be too rapid so as to avoid appreciable evolution of hydrochloric acid, which might carry with it some vapors of monomethyl dichlorosilane.

References cited by the Patent Office:

USPat 2,597,614 (Harris Research Labs/1952): see first paragraph of this digest.

USPat 2,473,497 (Gen Electric/1949): preparing polysiloxane resins by employing as hydrolysis medium mixtures of water, a hydrocarbon solvent (mineral spirits) and a solvent of the glycol ether type.

USPat 2,448,556 (Gen Electric/1950) relates to synthetic elastic polysiloxanes containing recurrent units of di- and monomethylsiloxanes.

USPat 2,511,296 (Montclair Research/1950) relates to agents for film-forming, molding, laminating, etc, which contain copolymerizates of a silicohaloform (silicochloroform) and methylsilicon halides in hydrolyzed form.

RELIEF-LIKE PRINTS——— Resin Dispersions Locally Precipitated D, 1

Brit P 696,578 (Heberlein & Co——Sept 2, 1953)

The use of hardenable resins heretofore has limited the printing effects on textiles to flat patterns only. The production of relief-like effects by printing from engraved rollers has been hampered by the limited depth of the engraving, generally poor adhesion of considerable amounts of plastic material to the fibers, and sticking of the paste in the deep grooves of the rollers.

These problems reportedly have been solved by using as the compound which forms the pattern effect a resin in dispersed state; it is precipitated in a second step. There are two alternatives: either the thickened precipitating solution is preprinted and the resin dispersion is subsequently applied, e g, by immersion, or the fabric is prepared with the precipitant and the resin dispersion is printed with deeply engraved rollers. In almost all the examples cited the first alternative is carried out. In this event the amount of resin to be precipitated may vary, especially according to the time of immersion.

All kinds of thermoplastic resins, e g, vinyl resins, synthetic rubber, cellulose esters, etc, can be dispersed using one of the customary emulsifiers. White or colored pigments or fillers may be stirred into this dispersion. The addition of flock fibers is particularly advocated because it improves the touch of the fabric, which otherwise becomes somewhat rubbery.

The precipitating agent is generally a salt of a polyvalent metal (Al, Pb, Fe, etc), or perchloric or aromatic sulfonic acids. The general principle of the patented method is to use a cation-active precipitating agent where an anionic emulsifier is present and vice versa.

Variations may also be brought about by employing engraved rollers of graduated depths, thereby producing shaded or half-tone effects and the like.

Example: A viscose crepe georgette fabric is printed with a paste of aqueous aluminum sulfate solution (1:1) thickened with an equal amount of crystal gum thickener 1:2, then dried and immersed at room temperature for two minutes in a polyacrylic resin dispersion, i e, Rhoplex WC9, diluted at a ratio 2:3 with water. The fabric is rinsed, dried without tension at 60° C and finally steamed on a tenter frame. Soft plastic patterns result. Other precipitating agents, e g, chromium chloride and lead acetate and polyvinyl butyral dispersions (D-1000), are mentioned in other examples.

Reference may be made to USPats 2,416,977-78 [cf *Am Dyestuff Reptr 36*, 366, (1947)] which cover Aspinook Corp's method of producing relief prints by preprinting cellulose resists and following with mercerizing shrinkage. In contrast to this and other relief-printing methods, the present method obtains this effect by mutual precipitation of two compounds so that the amount of one component (the resin) can be controlled by the concentration of the precipitant and by the time of immersion.

An earlier patent of Heberlein (USPat 2,233,609) refers to the patterned contrast effects obtained from pigmented resins, which are precipitated optionally in parchmentizing procedure. No relief-prints are claimed in this specification.

DYEING POLYACRYLONITRILE FIBERS———Cuprous-Ion Technique Applied under Acid Conditions C, 4, 07

Brit P 696,984 (Union Carbide & Carbon Corp——Sept 9, 1953)

Polyacrylonitrile fibers are generally dyed with insoluble acetate dyes, and although certain other (basic or acid) dyes can be applied at temperatures above 100°C under superatmospheric pressure, no satisfactory results can be expected from them on filaments containing over 60-70% acrylonitrile in the copolymers.

The present process uses the cuprous-ion effect[1] with certain modifications to the effect that pure polyacrylonitrile fibers or copolymers thereof with another monounsaturated compound can be dyed a dark shade, fast to washing and crocking. These modifications comprise treating the material at temperatures of at least 175°F (but not exceeding 212°F) at a pH of 2-4.5 (preferably at 2.7) in the presence of cuprous ions. Acid wool dyes, direct cotton dyes and water-soluble acetate dyes reportedly give very good results in dyeing the aforementioned polymer or copolymer fabrics, although this process does not help in dyeing cellulosic fibers or resinous fibers containing no polyacrylonitrile, e g, in vinyl-chloride-acetate copolymers (Vinyon). This can be proved by the dyeing behavior of mixed fibers, e g, cotton-polyacrylonitrile, where the dyes are taken up mostly by the acrylonitrile component.

After being scoured the fibers are treated in a second bath containing, in addition to dyestuff, a cuprous salt (usually prepared in situ from a cupric salt and a reducing agent), a swelling dye assistant, and an acid to bring the pH below 7.

Among the most effective swelling (dyeing) assistants are derivatives of diphenyl or benzylphenyl containing one OH-group; a preferred compound is p-phenylphenol, which has to be added in the solubilized state as sodium phenyl phenoxide and reconverted into finely divided p-phenylphenol upon acidifying.

Example: After being prescoured at room temperature for 10 minutes, an acrylonitrile-vinylchloride copolymer yarn is treated in a dyebath (ratio 30:1) containing 3% of sodium-p-phenylphenoxide, 3% of acetic acid, 1% of cupric sulfate, and 0.4% of zinc sulfoxylate-formaldehyde (all percentages calculated from the fabric's weight). Thereafter 5% of Cloth Red G (C I 249) is added and the bath temperature raised to the boil and maintained there for 90 minutes. After the yarn is scoured and dried at 248°F for 15 minutes a uniform full red shade of good wash- and crock-fastness results.

[1] This technique is discussed, among other sources, in *Chem Eng News* 28, 4268 (1950). Cf also digest to U S Pat 2,653,074 in *Am Dyestuff Reptr 43*, 383 (1954).

DYEING NYLON OR CELLULOSE ACETATE with Ice Colors———Guanidine Added C, 4, 07

Brit P 699,194 (Gen Aniline & Film Corp——Streck——Nov 4, 1953)

This patent was found to be parallel to USPat 2,649,353 [cf *Am Dyestuff Reptr 43*, 214 (1954)].

WATER-REPELLENT FABRICS——— Organosiliconhalides Applied on Predried Material G, 2, 02

Brit P 699,210 (Th Goldschmidt Akt Ges——Nov 4, 1953)

Numerous water-repellent-finishing methods based on organosilicon products, especially organosilicon halides, have been patented in the past. This group of hydrophobing processes has almost eclipsed former standard methods. Fixation of the organosilicon-halides is accomplished by a direct reaction of the halides with reactive groups (especially hydroxy groups), present either in the material to be treated or in a thin moisture film covering the fabric's surface. In this event, HCl is formed, and its impairing of the tensile strength of cellulosic fibers is all too well known. (Spun rayon reportedly loses up to 38% with 10 sec when exposed to vapors of the siliconhalides).

It has been observed that this fiber damage can be substantially avoided by strongly reducing the moisture content of the fabric to three (or preferably one) percent prior to the organosilicon halide treatment. Within the scope of the cur-

rent invention are organosilicon halides corresponding to the general formula R_aSiX_{4-a} (wherein "R" is alkyl, aryl or aralkyl, "a" is a number between 1 and 4, and "X" is halogen), and halides containing free H-atoms linked to Si. They can be used in vapor form as well as from solvent solutions for hydrophobing cellulosic and synthetic fibers, paper rolls and asbestos cloth. Predrying may be carried out in any conventional way, for instance, at 100°C at atmospheric pressure, up to 110-120°C under reduced pressure, or in a conditioning chamber. Fibers subjected thereupon to the organosilicon halide treatment are found to be but slightly degraded.

Example: Spun rayon of 11% mositure content is dried in a chamber at 105° C until the moisture content has been reduced to about 1%. Then the fibers are allowed to fall in form of small bundles through tubes filled with vapors of methylsilicon chloride, the reaction time being between 5 to 10 seconds. Finally the material is spread out in shallow layers and dried, optionally in a dry air current or in vacuo to remove adherent vapors of hydrochloric acid and methylsilicon chloride.

Reference is made to USPat 2,306,222 of Patnode, one of the first patents in this field, which describes hydrophobing with methylsiliconchloride vapors. The inventor in this patent proposed that the fabrics be dried to remove surface moisture, then exposed to the vapors of the aforementioned agent and finally, to ammonia vapors. This is in contrast to the present process in which predrying apparently is carried out to a higher and well-controlled degree, and neutralization with ammonia is omitted.

OBITUARY

The late A R Chantler

AMBROSE R CHANTLER, retired Du Pont official and one of the deans of the American dye industry died in Delaware Hospital, Wilmington, Del, July 28, after a long illness. He was 61 years old.

Mr Chantler, one of the first of the young men who grew up with the American dye industry at its start in World War I, was particularly active throughout his career in the development of vat colors and in expanding their use in the printing and finishing industries. In World War II, he served on the Dyestuffs Industry Advisory Committee to the War Production Board and devoted much of his personal time to the application of fast colors for all types of military equipment. During 1952 he served as president of the Synthetic Organic Chemical Manufacturers' Association.

Born in Pawtucket, Rhode Island on August 26, 1892, he received his B S degree in chemical engineering from Rhode Island State College in 1916. After service in the army in World War I, he joined the U S Finishing Company, in Providence, R I, as a textile chemist. In 1919 he went with Du Pont as a dye salesman in their Providence office and, after 5 years, was appointed assistant director of sales in the dyestuffs division. He was named director of sales in 1929 and served in that capacity for over 20 years until he was made sales advisor for the organic chemicals department in June of 1950. He retired in 1952.

Perkin——

(Concluded from page 519)

could be made from the vile-smelling coal tar or with the chemists who worked with these "wastes."

Perkin remained aloof from all controversy and he had no political aspirations. His only interest in his commercial venture was to obtain enough money to devote his life to "pure research." Perhaps the character of this great but simple man may be summed up in the words of a well-known writer:

"He was a blameless Christian, a perfect gentleman, a fine type of the old conservative, he lived unobtrusively, worked quietly and intensively, worshipped God, and respected his neighbor. To us living in days of turmoil and upheaval such a personnage already belongs to an age long past."

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(2) Perkin, W H, "The Origin of the Coal-Tar Industry, and the Contributions of Hofmann and His Pupils", *J Chem Soc* 69, 556 (1886).

(3) Meldola, R, "Perkin Obituary Notice", *J Chem Soc* 93, 2214 (1908).

(4) Harrow, B, "Eminent Chemists of Our Time", New York (1927).

(5) Reiman, M, "On Aniline and Its Derivatives". A treatise upon the manufacture of aniline colours, to which is added, in an appendix 'The Report on the Colouring matters derived from coal tar', shown at the French Exhibition, 1867, by Dr A W Hofmann, Mm G DeLaire, and Ch Girard. The whole revised and edited by William Crookes, London (1868).

(6) Crookes, W, "A Practical Handbook of Dyeing and Calico Printing", London (1874).

(7) Miall, S, "A History of the British Chemical Industry", London (1931).

GENERAL CALENDAR

AMERICAN CHEMICAL SOCIETY
National Chemical Exposition—Oct 12-15, Chicago, Ill.

AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS
Southern Textile Conference—Nov 4-5, North Carolina State College, Raleigh, N C.

AMERICAN SOCIETY FOR QUALITY CONTROL
Annual meeting, Textile Div—Jan 27-29, Clemson College School of Textiles.

CHAMBRE SYNDICALE TRAMAGRAS
International Detergent Congress—Aug 30-Sept 5, The Sorbonne, Paris, France.

DELTA KAPPA PHI FRATERNITY
1955 Annual Convention—April 29-30, Lowell, Mass.

DEUTSCHE GESELLSCHAFT FUR CHEMISCHES APPARATEWESEN
Achema XI—May 14-22, Frankfurt am Main, Germany.

THE FIBER SOCIETY
Fall Meeting—Sept 13-14, McGill University, Montreal, Canada.
Spring Meeting—May 4-5, 1955, Alabama Polytechnic Institute, Auburn, Alabama.
Fall Meeting—Sept 8-9, 1955, Massachusetts Institute of Technology, Cambridge, Mass.

INTERNATIONAL CONGRESS OF INDUSTRIAL CHEMISTRY
27th Congress—Sept 11-19, Brussels, Belgium.

INTERNATIONAL TEXTILE EXHIBITION
2nd Exhibition—June 25-July 10, 1955, Brussels, Belgium.

INTERNATIONAL WOOL TEXTILE RESEARCH CONFERENCE
September, 1955—Sydney, Melbourne, and Geelong, Australia.

NATIONAL ASSOCIATION OF HOSIERY MANUFACTURERS, KNITTED OUTERWEAR ASSOCIATION, THE UNDERWEAR INSTITUTE
42nd Knitting Arts Exhibition—April 25-29, Convention Hall, Atlantic City, N J.

NATIONAL COTTON COUNCIL OF AMERICA
1954 Chemical Finishing Conference—Oct 7-8, Hotel Statler, Washington, D C.
Annual Meeting—Jan 31-Feb 1, Hotel Shamrock, Houston, Tex.
Cotton Research Clinic—Feb 16-18, Pinehurst, N C.

NATIONAL INSTITUTE OF DRYCLEANING
4th Educational Conference—Dec 5-10, Silver Spring, Md.

NORTH CAROLINA TEXTILE MANUFACTURERS ASSOCIATION
48th Annual Meeting—Oct 14-15, The Carolina, Pinehurst, N C.

SOUTHERN TEXTILE EXPOSITION
October 4-9 (Textile Hall, Greenville, S C).

TEXTILE RESEARCH INSTITUTE
25th Annual Meeting—March 10-11, Hotel Commodore, New York, N Y.

TEXTILE TECHNICAL FEDERATION OF CANADA
4th Seminar—Sept 9-11, Queen's Univ, Kingston, Ont.

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